

Mechanochromophore-Linked Polymeric Materials with Visible Color Changes

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Mechanical force as a type of stimuli for smart materials has obtained much attention in the past decade. Color-changing materials in response to mechanical stimuli have shown great potential in the applications such as sensors and displays. Mechanochromophore-linked polymeric materials, which are a growing sub-class of these materials, are discussed in detail in this review. Two main types of mechanochromophores which exhibit visible color change, summarized herein, involve either isomerization or radical generation mechanisms. This review focuses on their synthesis and incorporation into polymer matrices, the type of mechanical force used, factors affecting the mechanochromic properties, and their applications.

1. Introduction

Chemical reactions can be categorized into photochemistry, thermochemistry, electrochemistry, and mechanochemistry based on the source of energy.^[1] Mechanochemistry is relatively new among these categories but has been developed intensively in recent years.^[2] Application of an external force can selectively impact the weak bonds in a molecule, leading to chemical activations such as decomposition reactions and radical generation upon bond cleavage.^[3] Molecules that undergo structural changes triggered by mechanical force are referred to as mechanophores.^[4,5] Either bond cleavage or isomerization of the mechanophore occurs when the weak bonds or strained rings on the molecules are subjected to force. When the mechanophores are covalently linked to polymer chains, the functional groups generated from mechanical activation provide

possibilities for a range of chemical reactions. For example, the ortho-quinodimethide resulting from the mechanophore benzocyclobutene under stress can react with bismaleimide to form a gel.^[6,7]

More specifically, when the mechanical activation of mechanophores is accompanied by an optical change in absorption (visible color) or emission (fluorescence and luminescence), the molecules are referred to as mechanochromophores.^[8] The mechanochromophores exhibiting visible coloration mainly include ring-opening (isomerization) and radical generation-based mechanisms.^[4,8–10] Isomerization-

based mechanochromophores consist of a spiro-junction that undergoes ring-opening under external force, resulting in resonance structures causing a change in color (**Figure 1**). Mechanochromophores of spiropyran (SP),^[11] spirothiopyran (STP),^[12] rhodamine (Rh),^[13,14] and naphthopyran (NP)^[15,16] are within this ring-opening category. The processes of ring-opening and ring-closure are reversible upon loading and unloading of force. The bond breaking mechanism and incorporation of these mechanochromophores into a range of polymer matrices for stress/strain sensing purposes have been widely studied, whereas the radical generating mechanochromophores are less reported in applications of macroscopic visualization. Radical-based mechanochromophores contain a dynamic C–C “bridge” connecting two identical moieties and go through a homolytic bond cleavage under deformation. This leads to radical formation at the bridge accompanied by a color change. Radical-based mechanochromophores include diarylbibenzofuranone (DABBF),^[17–20] diarylbibenzothiophenonyl (DABBT),^[21,22] tetraarylsuccinonitrile (TASN),^[23–25] and difluorenylsuccinonitrile (DFSN),^[26] with DABBF being the most reported. The reversible reaction of dissociation and recombination of the dynamic C–C bond not only enables the properties of color switching, but also provides great opportunities for use as self-healing agents.^[20,27,28]

In addition to these two main types of mechanochromophores exhibiting visible color changes, there are mechanophores generating fluorescence or chemiluminescence upon bond cleavage. For example, maleimide-anthracene cycloadducts release anthracene and maleimide species upon bond scission, with only the former producing fluorescence.^[29,30] An anthracene-dimer mechanophore can generate two emissive anthracenes upon loading and they can reversibly dimerize triggered by UV irradiation.^[31,32] 1,2-dioxetane, a chemiluminescence mechanophore, breaks into two ketones under stimuli,

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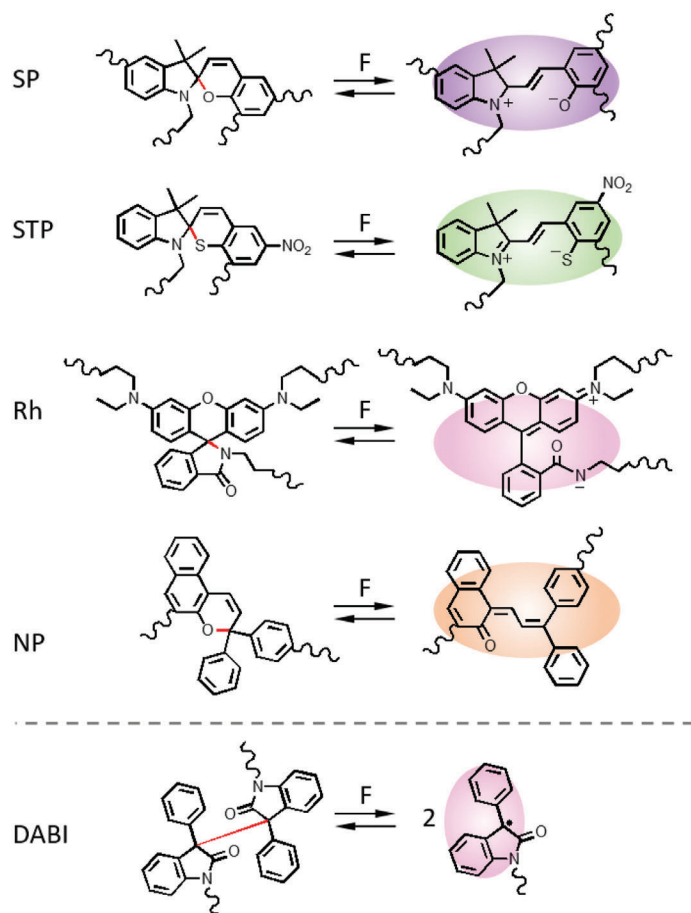
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Isomerization-based mechanochromophores



Radical-based mechanochromophores

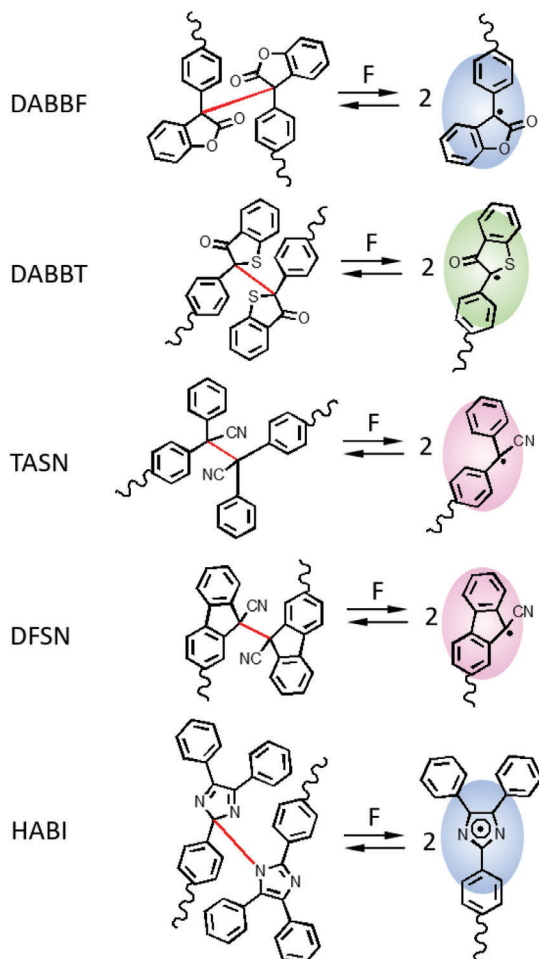


Figure 1. Chemical structures of the reported polymer conjugated mechanochromophores, either isomerization-based or radical-based, and their bond cleavage reactions under force. The mechanically weak bonds are labeled in red.

showing a blue luminescent color.^[33,34] The chemiluminescence occurs due to one of the decomposed moieties relaxing from an electronically excited state to the ground state. Unlike the above-mentioned mechanochromophores with reversible color-changing behavior, the light emission process of luminescent mechanochromophores is irreversible.^[33]

This review will focus on the two main types of mechanochromophores generating visible color changes (isomerization-based and radical-based) and their covalently linked polymers, including the synthetic approaches, categories of triggering force, elements affecting the mechanochromic activity, and their potential applications. Some examples will be repeatedly introduced in different sections with an emphasis on their synthesis, polymer architecture, or aspects influencing their mechanochromic performance.

1.1. Isomerization-Based Mechanochromophores

Among the first class of mechanochromophores which involve either C–O, C–N, or C–S bond breakage of a bicyclic strained

structure, to form a conjugated colored species, SP has been the most reported (Figure 1). SP was originally reported in 1963 for its thermochromism^[35] and has since been widely investigated for its photochromic properties.^[11,36–41] It was not until 2007 that SP covalently linked to polymer in solution was found to undergo a color change when subjected to a mechanical force induced by ultrasound.^[42] In 2009, the first mechanochromic SP covalently linked bulk polymer was reported by the Moore group,^[43] which opened the door to an intensive exploration of the mechanochromic properties of SP. Upon activation, colorless SP converts into a purple-colored and ring-opened isomer merocyanine (MC).^[11,44–46] This isomerization process demonstrated great potential for a range of applications, not only because of the resulting optical change but also the different physical and chemical properties between SP and MC. Optically there is no absorption signal in the visible range for colorless SP, whereas MC shows a strong absorption peak at 500–600 nm. Likewise, no fluorescence is generated from SP while MC shows fluorescence. SP is a highly hydrophobic molecule, whereas MC is more hydrophilic, enabling them to be used in the fields of self-assembly,^[47,48] drug delivery,^[49,50]

and wettability control and cell adhesion.^[51,52] The increase in molecular size during the transition from SP to MC has been used for microfluidic applications.^[53,54] The transition from a neutral to charged molecule has been applied for metal ion detection^[55,56] and electrochemistry.^[57,58] Most of these applications rely on light control, benefiting from the photochromism of SP. The equilibrium between SP and MC is affected by the polarity of the environment, whereby under polar conditions the more hydrophilic MC is stabilized, even without UV stimulus, which has been defined as negative photochromism.^[59–61] A polar environment can be afforded by either the solvent,^[62] bulk material,^[63] or the attached polymers.^[64] Multi-responsive and functional materials can be obtained by combining the photochromic and thermochromic properties of SP.^[65,66]

Rh has been widely reported for its fluorescent properties and is used as pigments, chemosensors, and fluorescent probes in the fields of imaging, biological detection, and molecular devices.^[67,68] Rh is a spiroactam-based compound and undergoes a ring-opening reaction triggered by external stimuli to form an isomer with optical features of absorption (pink color) and fluorescence emission. The stimuli can be afforded by acidification,^[69,70] metal ions,^[71,72] or force.^[13,14] The non-fluorescent ring-closed Rh is a bicyclic-spiro structure while the ring-open isomer is a planar zwitterionic amide with high quantum yield.

NP is a pyran-based compound and was initially investigated for its photochromism, while its mechanochromic properties were found much later.^[15] Upon exposing NP to a stimulus, such as UV light irradiation or force, the C–O bond undergoes an electrocyclic ring-opening reaction, resulting in the colorless NP isomerizing into an orange-colored merocyanine.

The chemical structure of STP is similar to SP, with a C–S bond at the spiro-junction in STP rather than a C–O bond. When the C–S bond of STP (pale yellow) breaks with stimuli, such as temperature, UV light, or force, the molecule isomerizes to ring-opened thiomercyanine (TMC) which is green in color.^[73–74]

1.2. Radical-Based Mechanochromophores

The second class of mechanochromophores results in the generation of radical species from the cleavage of a C–C bond or a bis-aryl structure (Figure 1). The radicals generated from DABBF dissociation are blue, and the dynamic equilibrium between DABBF and the reversible process were used for self-healing purposes before their properties of mechanochromism were discovered.^[20] The color of DABBT derivatives changes from colorless to green upon radical generation from the dissociation of the dynamic C–C bond.^[21,22] TASN derivatives turn from colorless to pink upon C–C dissociation triggered by heat or mechanical force.^[23,75] DFSN is a radical-based mechanochromophore with a higher thermostability compared to the others in this class.^[26] Pink radicals are generated from the dissociated DFSN under external force, accompanied by new absorption peaks at 542 and 526 nm, and the mechanochromophores can resist heating up to 130 °C. These four radical-based mechanochromophores have been well studied by the Otsuka group.

Diarylbiindolinone (DABI) is structurally analogous to DABBF, with the dynamic C–C bond-forming part of a lac-

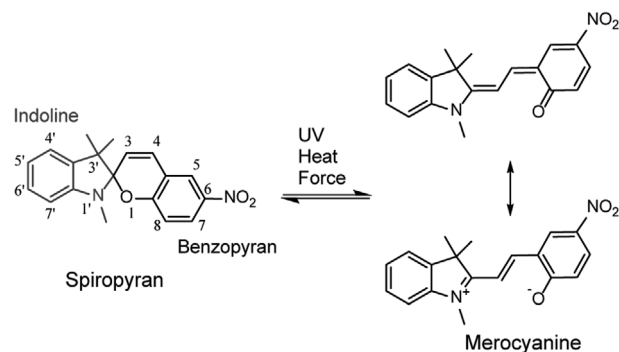


Figure 2. Chemical structure of SP and its ring-opening reaction under external stimuli.

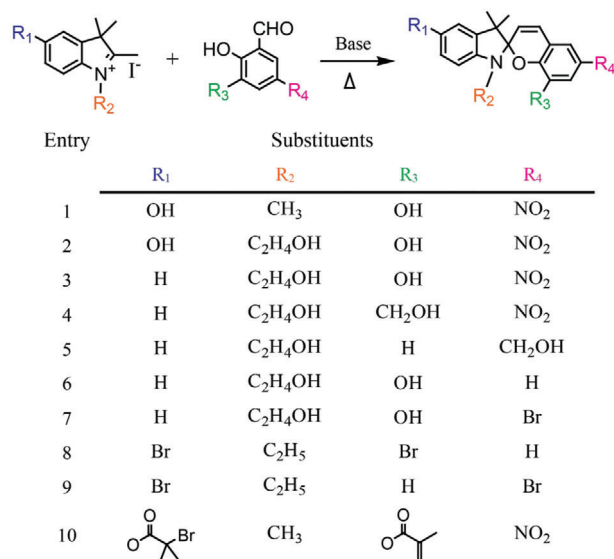
tam instead of a lactone ring.^[76] The powder of white-colored DABI derivatives switch to pink upon grinding, due to the breakage of the dynamic C–C bond. Inspired by the photoinitiator of triphenylimidazolyl (TPI) radicals which are generated from dissociated hexaarylbiimidazole (HABI) in response to UV light irradiation^[77] and the radical-based mechanochromophores reported by the Otsuka group,^[17] the properties of mechanochromism and initiating radical polymerization upon bond cleavage of HABI were investigated by Verstraeten and co-workers.^[78] A dynamic C–N bond connects two identical imidazole rings to form a HABI molecule, which is different from the other radical-based mechanochromophores with a dynamic C–C bond. The conversion from HABI to TPI can also be triggered by heat, light, or force, and the response to light has been used for self-healing.^[79,80] The generated TPIs upon C–N bond cleavage endow the polymeric materials with a blue color.

2. Synthesis of Mechanochromophores, Integration into Polymeric Matrices, and Bulk Material Processing

2.1. Isomerization-Based Mechanochromophores

SP Synthesis: SP molecules consist of an indoline ring and a benzopyran moiety, which are connected perpendicularly via a weak C–O bond (**Figure 2**). MC can be in a zwitterionic or quinoidal form, and both forms exist during activation. Ring-closure of MC is a thermodynamic process which occurs upon release of the stimuli. For mechano-responsive SP polymeric materials, both the indoline ring and the benzopyran moiety are required to be attached to polymer chains, so that the applied force can be transferred along the C–O bond, resulting in its cleavage. This principle is used with other mechanochromic responsive compounds, with polymer attachment being designed at opposite sides of the weak bond. There are several linkage points on the SP molecule, where polymer chains have been attached, with the 5'- or 1'-position on the indoline side and 8- or 6-position on the benzopyran side (**Scheme 1**).

Covalently bonded SP polymeric materials can be prepared using several common methods. For the synthesis of SP molecules, the last step is a condensation reaction of salicylaldehyde derivatives and indolium salts under basic conditions (**Scheme 1**).



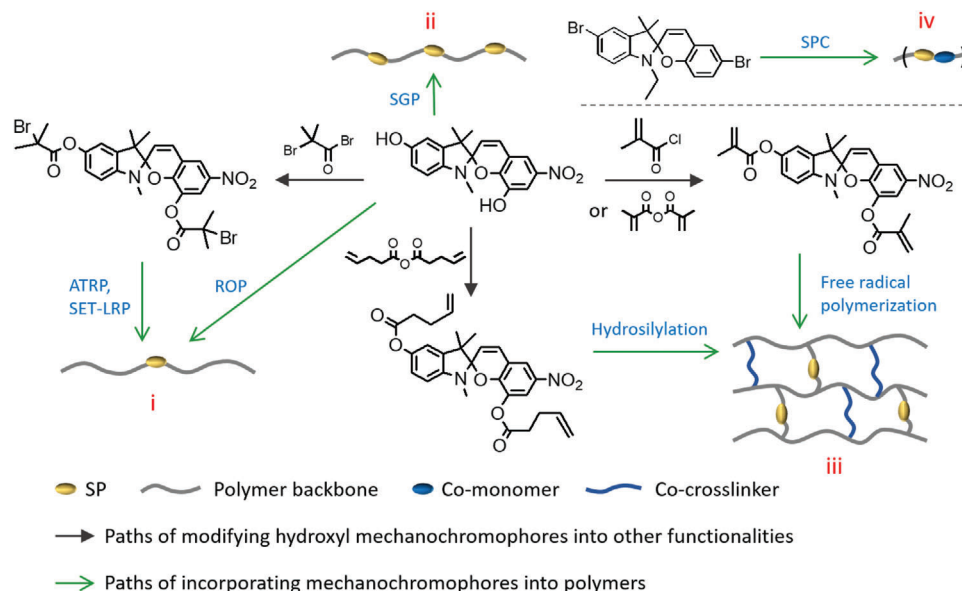
Scheme 1. Synthesis of SPs with different substituents from indolium salts and salicylaldehyde derivatives via condensation reactions.

Accordingly, the functional groups on the obtained SP are originally from salicylaldehyde and indolium salts.

6-Nitro-SP mechanophores have been widely used, and the most common functionalities were hydroxyl groups at the 5'- and 8-positions (SP_{5',8-OH}).^[43,81,82] The functional group on the indoline moiety can also be attached at the 1'-position, by conjugating 2-iodoethanol to the indolium to form a salt, prior to condensation (SP_{1',8-OH}).^[83–85] Tri-hydroxyl SP was synthesized through combining the attachment at the 1', 5'- and 8-positions (SP_{1',5',8-OH}).^[86] SP without a nitro group at the 6-position has also been synthesized and is UV inactive due to the absence

of a strong electron-withdrawing group. Salicylaldehyde derivatives without a nitro group, but with an alkyl alcohol group at the 6-position reacted with indolium salts with alkyl alcohol at the 1'-position to afford di-hydroxyl SP (SP_{1',6-OH}).^[87] Other functionalities, such as alkyl bromide and methacryloyl ester groups, can also be introduced before the condensation step through modifying the salicylaldehyde and indoline derivatives. Jia et al. synthesized indoline derivatives with an alkyl bromide group and salicylaldehyde derivatives with a methacryloyl ester group, which reacted to afford SP consisting of different functional groups at the 5'- and 8-positions (SP_{5',8-Br-MA}).^[88] A 6-bromide-SP with hydroxyl functionalities at the 1'- and 8-positions was synthesized,^[89] as well as 6-nitro-SP and 6-hydrogen-SP.^[90] SP with bromide groups at the 5'- and 8-positions was synthesized from indolium salts and salicylaldehyde derivatives with bromide groups by Sommer's group (SP_{5',8-Br}).^[91] A similar SP with iodide groups (SP_{5',8-I}) was reported earlier in 2006 for photochromism.^[92] For a different attachment position on the indoline moiety, SP with bromide groups at the 5'- and 6-positions was reported (SP_{5',6-Br}).^[91,93–96]

The hydroxyl groups on SP are sites for further modification with other functional groups facilitating incorporation into different polymers, including methacryloyl ester groups, alkene groups, and bromoisobutyroxy groups (**Scheme 2**). The modification of hydroxyl to methacryloyl ester groups has been achieved by nucleophilic addition with methacryloyl chloride^[43] or esterification with methacrylic anhydride.^[81] Triethylamine (TEA) was a commonly used base and the catalyst was 4-(dimethylamino)pyridine (DMAP). Despite that, the addition of TEA can be unnecessary. The amount of DMAP equivalent to 0.9 of hydroxyl groups can maintain basic conditions, leading to esterification occurring in high yields.^[97,98] The stringent reaction conditions of methacryloyl chloride with TEA as base involved low temperature (ice bath) and dropwise addition to control the



Scheme 2. Modification of hydroxyl SP (SP_{5',8-OH} as an example) into other functional groups, and the functionalized SPs as initiators, monomers, or cross-linkers can be integrated into polymers via different polymerization approaches to afford i) linear polymer with a single SP centered in a polymer chain, ii) linear polymer with multiple SPs along a polymer backbone, iii) cross-linked polymer, and iv) linear polymer with alternating SP and co-monomer.

reaction speed. The reaction using anhydride without TEA was more moderate; neither ice bath nor dropwise addition was required. Craig's group has reported this method to functionalize SP_{1,8-OH} with alkene groups.^[84]

One of the challenges of modifying di-hydroxyl SP is converting the target product to its ring-closed form. The basic conditions of the reaction push the equilibrium SP $\leftrightarrow$ MC towards MC and the polar eluent of the chromatography also favors MC due to solvatochromism. The product in the MC form can possibly aggregate because of the zwitterionic structure and π -stacking,^[11] and degrade because of oxidation and radical attack;^[99,100] thus, the ideal form for storage is the ring-closed version. The most common approach was recrystallization of the obtained functional molecules in hexane after column chromatography.^[43] The drawbacks of recrystallization include a longer purification time and lower yields. Attempts have been made to avoid the recrystallization step. For example, after column chromatography, increasing the ratio of non-polar solvent during the rotary evaporation provided pure alkene functionalized SP.^[101]

With the functional groups attached, SP can be incorporated into various polymers. A range of basic polymerization methods has been utilized, including free radical polymerization (photo or thermal), atom transfer radical polymerization (ATRP), step-growth polymerization (SGP), ring-opening polymerization (ROP), hydrosilylation, reversible addition-fragmentation chain transfer polymerization (RAFT), and Suzuki polycondensation (SPC).^[102] SP has been covalently linked into linear polymer backbone as an initiator via ATRP, ROP, and RAFT, resulting in a single SP centered in a polymer chain, or as a monomer to form multiple SPs embedded along a polymer chain by SGP and SPC; when SP functions as a cross-linker, the polymer networks can be prepared via free radical polymerization and hydrosilylation (Scheme 2). Linear polymers containing SP were normally obtained in powder form after a precipitation step, followed by hot pressing to fabricate bulk samples. Cross-linked SP polymers were generally obtained in bulk and the polymerization occurs within a mold.^[43] The isomerization-based mechanochromophore-linked polymeric materials reported in the literature are summarized in **Table 1**, along with their activation sources, analytical methods, and threshold strain/stress for color activation. It should be noted that the values of threshold stain/force are only for reference but not a direct comparison due to different testing methods and conditions.

Linear polymers with a single SP centered in the chain: Difunctional SP mechanochromophores have been reported where a central SP moiety has been functionalized with two pendant polymer chains. In the first example, SP with α -bromo ester groups was reacted with methyl acrylate under ATRP conditions to afford SP-PMA. This linear polymer was processed into a bulk sample by hot-compression in a mold at 54 °C.^[43,111,112] Similarly, linear SP-poly methyl methacrylate (PMMA) was synthesized using a copper-based-ATRP method with 2,2'-bipyridine as a ligand and a molecular weight up to 260 kDa.^[110,111] In another report, centrifugal force spinning was used to process SP-PMA linear polymers.^[143] SPs embedded in various polyacrylates were also prepared by ATRP of α -bromo ester SP initiators (**Figure 3A**).^[113] SP-linked polystyrene (PS) has also been reported.^[114] Compression molding and spin coating were employed to prepare bulk samples and thin films respectively.

Weng's group designed a triblock copolymer bearing SP in the chain center.^[85] Difunctional α , ω -bis-bromo ester SP as an initiator was first polymerized with *n*-butyl acrylate (*n*BA) via ATRP, followed by conjugation with PS blocks (**Figure 3B**). The molecular weight of PS blocks was adjusted with a constant poly *n*-butyl acrylate (*Pn*BA) length to vary the ratio of soft and hard blocks. Bulk samples were obtained by solvent casting. Wang et al. synthesized an SP-linked amphiphilic triblock copolymer via single-electron-transfer living radical polymerization (SET-LRP) and ATRP.^[115] SP was conjugated with hydrophobic tert-butyl acrylate (*Pt*BA) before polymerization with temperature-sensitive *N*-isopropylacrylamide (NIPAM), leading to an amphiphilic block copolymer (**Figure 3C**).

Di-hydroxyl SP as an initiator was polymerized with ϵ -caprolactone (CL) via ROP, leading to one SP molecule centered in a polymer chain (**Figure 3D**).^[83] The beige-colored SP-PCL powder with M_w 60 kDa was obtained by precipitation in cold methanol after ROP, and processed into thin sheets by hot-pressing. Peterson and co-workers made use of 3D-printing technology to fabricate SP-PCL bulk samples.^[116] Two di-hydroxyl SPs, SP_{1,8-OH} and nitro-absent SP_{1,6-OH}, were integrated into poly ϵ -caprolactone (PCL) (M_w 90 and 82.5 kDa), followed by processing with commercial PCL filaments through melt extrusion, under a processing temperature of 110 °C. This demonstrated the capability of constructing special designs via 3D-printing to manufacture SP-based mechanochromic polymers, especially bulk materials, into irregular shapes. Yenpech et al. molded the linear SP-PCL with four-arm PCL at a lower temperature of 60 °C.^[117]

Linear Polymers with Multiple SPs along the Backbone: Di-hydroxyl SP can be incorporated into a polyurethane (PU) backbone as a monomer by SGP, resulting in a linear copolymer with multiple SPs distributed in the polymer chain. Generally, SP-diols react with excess diisocyanate as hard segments, then the isocyanate end groups react with polyether polyol as soft segments, followed by coupling with chain extender to afford SP-PU elastomers. Since isocyanate is highly sensitive to water, all the raw materials are required to be anhydrous with the bulk samples prepared under an inert atmosphere. Moore's group has utilized diphenyldiisocyanate (MDI) as hard segments to conjugate SP_{5,8-OH}, poly(tetramethylene glycol) (PTMG) (M_n = 650) as soft segments and hexamethylene diisocyanate (HDI) as chain extenders to prepare SP-PU elastomers (**Figure 4A**).^[119] SP integrated into either soft or hard segments of PU were synthesized,^[120] while PEG 200 has also been used as soft segments.^[121]

The Weng group has focused on synthesizing SP-PU with physical interactions such as hydrogen bonding. Ureidopyrimidinone (UPy) motifs functionalized with amine and hydroxyl groups were introduced into SP-PU backbone as chain extenders (**Figure 4B**).^[122] The resultant polymer was molded into thin films by solvent casting. The location of UPy was then adjusted by being end-capped in the PU chain through a reaction of mono-amine functionalized UPy with isocyanate functionalized SP-PU prepolymers.^[123] Chemical cross-linking was also introduced into the SP-PU elastomer to form a dual cross-linked elastomer, making use of the physical cross-linking (hydrogen bonding) from Upy dimers.^[124] Prepolymer of SP reacting with UPy-diisocyanate, HDI, and PTMG was cross-linked with poly(lactic acid) end-capped pentaerythritol (**Figure 4C**) in a Teflon mold to give bulk samples. Additionally, the Weng group

Table 1. A summary of isomerization-based mechanochromophore-linked polymeric materials.

Mechanochromophore	Role of mechanochromophore	Polymer	Approach	Architecture	Activation source	Analytical method	Threshold strain/force	Ref.
Spiropyran	Cross-linker	PMMA	Free radical	Cross-linked	Tension, compression, shear	RGB, fluorescence imaging	-	[43, 103–105]
		P(AM-co-MA/SP) hydrogels			Tension	RGB, UV-vis	>100%	[106]
		PEVA, PEOC			Tension	RGB	175%	[107]
		PHEA			Swelling	Absorption measurement	-	[97]
		Polyacrylates multinetwork			Tension	RGB	39%	[98]
		PEA multinetwork			Tension	RGB	≈50%; 400%	[108, 109]
	Initiator	PMA	SET-LRP	Linear, single SP	Tension	RGB	-	[43]
		PMMA	ATRP	Linear, single SP	Tension	Fluorescence imaging	-	[110, 111]
		PMA			Tension, ultrasound	Fluorescence imaging, UV-vis	≈375%	[43, 111–113]
		PEA, PnBA, PiBA, PzBA			Ultrasound	UV-vis	-	[113]
		PS			Laser pulse	Fluorescence imaging	-	[114]
		PS-PnBA-SP-PnBA-PS		Triblock copolymer, single SP	Tension	Optical images	-	[85]
		PNIPAM-PzBA-SP-PzBA-PNIPAM		Linear, single SP	Ultrasound	UV-vis	-	[115]
		PBA-SP-PS		Graft copolymer	Tension	RGB	54%	[88]
		PCL	ROP	Linear, single SP	Tension	UV-vis	39%	[83, 116]
		PCL		Cross-linked	Tension	RGB	10–30%	[117]
	Monomer	P(SP-co-epoxidized cyclooctadiene)	ROMP	Linear, multiple SP	-	Single molecule force spectroscopy	240–260 pN	[89, 118]
		PU	Step grow polymerization	Linear, multiple SP	Tension	UV-vis, fluorescence imaging	-	[119–121]
		PU-UPy			Tension	UV-vis	400%	[122, 123]
		PU-UPy		Cross-linked	Tension	RGB	400%	[124]
		PU-BTP		Linear, multiple SP	Tension	Optical observation	500%	[125]
		Waterborne PU			Ultrasound, tension	UV-vis	500%	[126]
		Bio-based waterborne PU			Tension	UV-vis	-	[127]
		POSS-PU		Cross-linked	Tension	UV-vis	700%	[128]
		PDMS		Linear, multiple SP	Tension	UV-vis	-	[129]

(Continued)

Table 1. (Continued).

Mechanochromophore	Role of mechanochromophore	Polymer	Approach	Architecture	Activation source	Analytical method	Threshold strain/force	Ref.
		P(SP- <i>alt</i> -F8)	Suzuki polycondensation	Linear multiple SP	Ultrasound	NMR spectra	-	[91]
		Polyarylene			Tension	RGB	-	[95]
		P(SP- <i>alt</i> -C ₁₀)			Embossing	Optical observation	-	[94]
		P(SP- <i>alt</i> -C ₁₀) nanofiber			Tension	RGB	>5%	[96]
		Polycarbonate			Tension	Fluorescence imaging	/	[130]
	Cross-linker	PDMS	Hydrosilylation	Cross-linked	Tension	RGB	≈90%	[84, 86, 131–134]
	Initiator	PBA-SP-PS	RAFT	Graft copolymer single SP	Tension	RGB	54%	[88]
	Monomer	PU	Step grow polymerization	Linear, multiple SP	Pressing	Emission measurement	125 MPa	[13]
	Cross-linker	PEA multinetwork	Free radical	Cross-linked	Tension	Emission measurement	24%	[14]
		PnBA			Tension	Emission measurement	-	[135]
Rhodamine		P(AM-co-MA-co-C18/Rh) hydrogels			Tension	Emission measurement	200%	[136]
		P(NaAMPS-co-DMAAm/Rh) hydrogels			Tension, freezing	Emission measurement	198%	[137]
		P(AMPS/Rh)-P(DMAA-co-AA) double network			Tension, compression	Absorption measurement	-	[138]
	Cross-linker	PDMS	Hydrosilylation	Cross-linked	Tension	Absorption measurement	-	[16]
		PDMS			High-intensity focused ultrasound	Optical observation	-	[139]
	Initiator	PDMS			Tension	RGB	-	[140]
Naphthopyran		PBA-silica composite	ATRP	Linear, single SP	Kneading	Absorption measurement	-	[141]
	Monomer	PES	Condensation	Linear, multiple SP	Ultrasound	Absorption measurement	-	[12]
		PU	Condensation	Linear, multiple SP	Tension	Absorption measurement	≈600%	[12]
	Monomer & initiator	PMA	Free radical & ATRP	Comb polymer	-	-	-	[142]

developed a healable SP-PU through incorporation of ligand 2,6-bis(1,2,3-triazol-4-yl)pyridine (BTP) into the polymer backbone, which formed complexes with metal ions (Figure 4D).^[125] Zn²⁺ or Eu³⁺ ions were used to construct metallo-supramolecular SP-BTP-PU polymers.

Jia et al. synthesized a waterborne SP-PU for mechanochromism.^[126] Dimethylolpropionic acid was in-

troduced into the polymer backbone constructed from SP, MDI, PTMG, and isophorone diisocyanate. The ionic waterborne PU formed an emulsion in water, which became a film after the water was removed. Afterward, SP-PU with an enhanced thermal aging stability was developed via employing polyhedral oligomeric silsesquioxanes (POSS) as a cross-linker.^[128] Wang et al. demonstrated an SP-containing bio-based water-

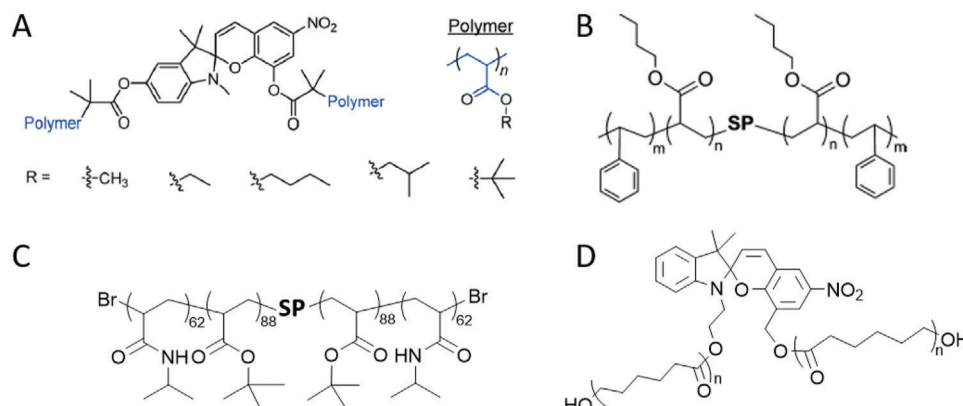


Figure 3. Linear polymers with a single SP centered in the polymer chains. A) SP linked in various polyacrylates via ATRP. Reproduced with permission.^[113] Copyright 2016, American Chemical Society. B) SP conjugated with PnBA and PS blocks via ATRP. Reproduced with permission.^[85] Copyright 2013, American Chemical Society. C) SP conjugated with PzBA and PNIPAM blocks via SET-LRP and ATRP. Reproduced with permission.^[115] Copyright 2015, American Chemical Society. D) SP-PCL via ROP. Reproduced with permission.^[83] Copyright 2010, American Chemical Society.

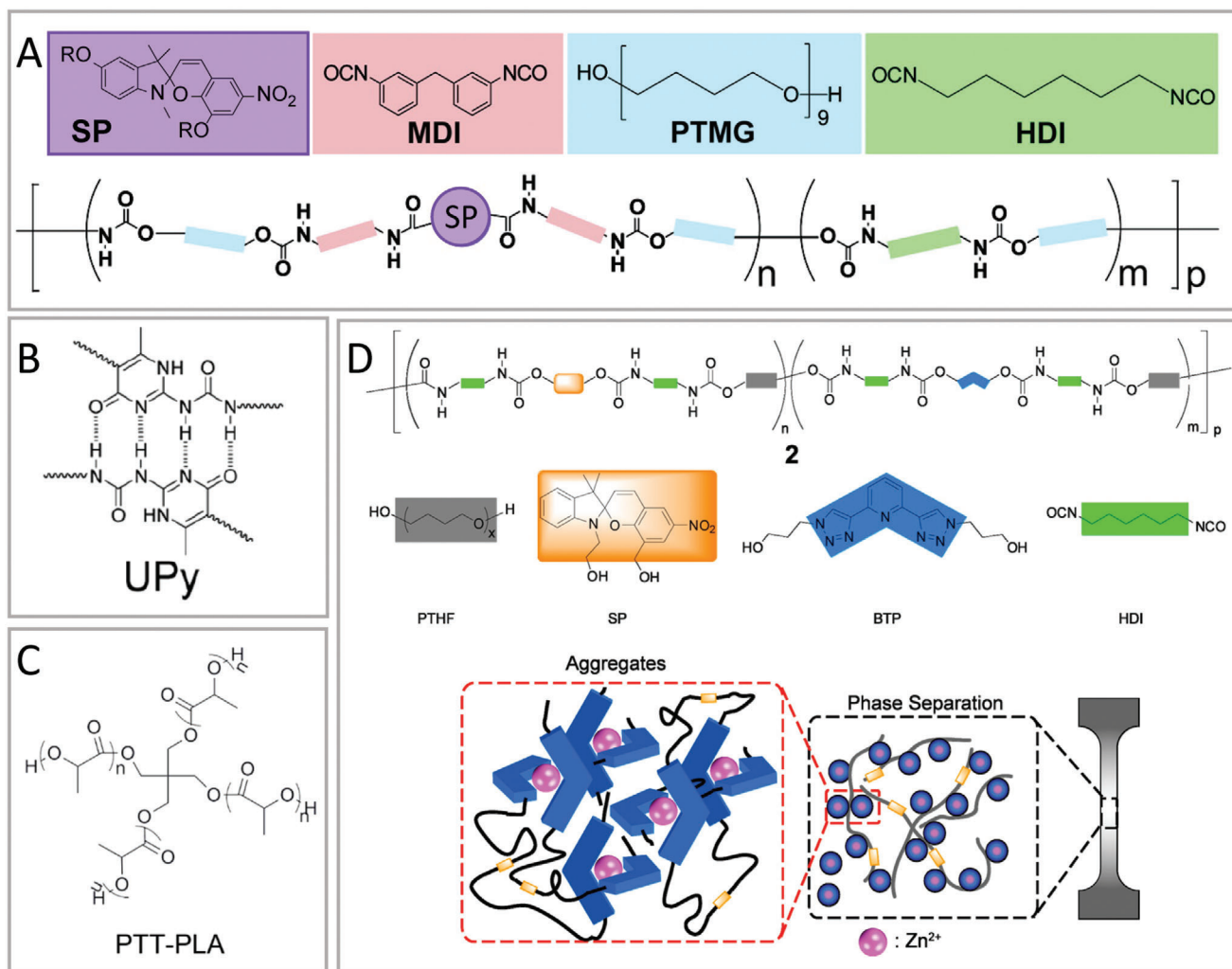


Figure 4. SP linked in PU backbone. A) SP integrated into PU via SGP where $m \gg n$. Reproduced with permission.^[119] Copyright 2010, American Chemical Society. B) Chemical structure of UPy motif and hydrogen bonding formation. C) Chemical structure of poly(lactic acid) end-capped pentaerythritol as a chemical cross-linker. D) BTP ligands incorporated into SP-PU backbone, leading to formation of metal-ligand complexes. Reproduced with permission.^[125] Copyright 2014, American Chemical Society.

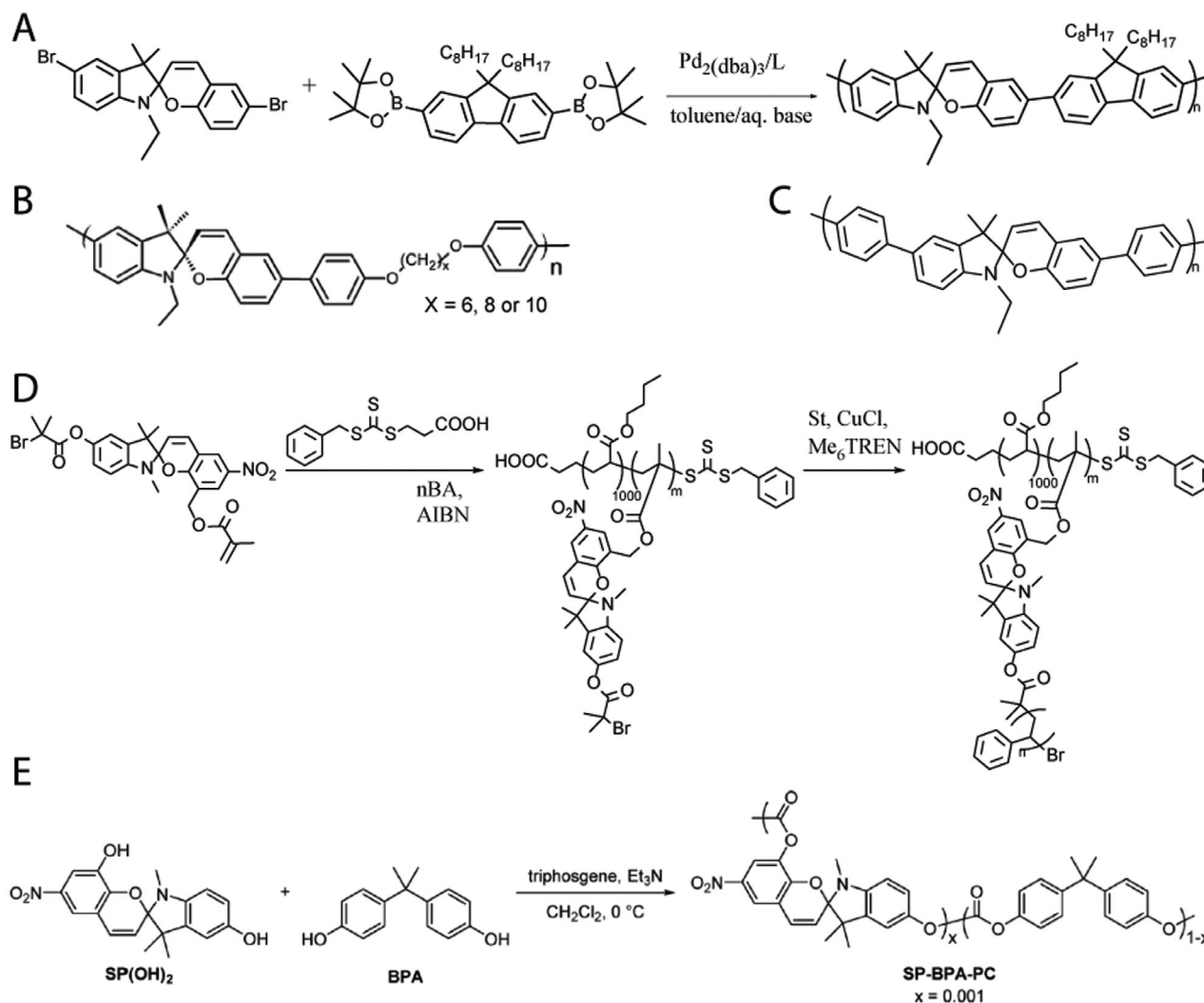


Figure 5. Linear polymers with multiple SPs along the backbone Suzuki polycondensation. A) Di-bromo SP copolymerizes with 9,9-dioctylfluorene. Reproduced with permission.^[91] Copyright 2013, Wiley-VCH GmbH. B) SP with phenol-based alkyl linker in 6–10 carbons. Reproduced with permission.^[93] Copyright 2014, The Royal Society of Chemistry. C) SP-linked polyarylene. Reproduced with permission.^[96] Copyright 2018, Wiley-VCH GmbH. D) Synthesis of comb-structured graft copolymer PnBA-SP-PS via RAFT and then ATRP. Reproduced with permission.^[88] Copyright 2018, Wiley-VCH GmbH. E) Synthesis of polycarbonate SP-BPA-PC via copolycondensation. Reproduced with permission.^[130] Copyright 2019, American Chemical Society.

borne PU for mechanochromism, where soybean oil modified with hydroxyl groups as polyols were used to synthesize the PU.^[127]

Di-bromo SP was synthesized to prepare polymers with alternating SP and stiff fluorene units via SPC.^[91] SP was copolymerized with 9,9-dioctylfluorene (F8) boronate ester using palladium catalyst to afford SP containing fluorene copolymers P(SP-*alt*-F8) (Figure 5A). In another work, a phenol-based alkyl linker (6–10 carbons) was alternately conjugated with SP via SPC to form P(SP-*alt*-C_x) where x represented the carbon number, as shown in Figure 5B.^[93] Later, microwave irradiation was used to assist the synthesis of P(SP-*alt*-C₁₀) , resulting in a molecular weight up to 174 kDa (M_n 34.8 kDa).^[94] An SP-linked polyarylene was also synthesized via Suzuki polycondensation (Figure 5C).^[95]

SP consisting of methacryloyl and bromo ester functionalities at the two ends was used as a monomer to polymerize with nBA

via RAFT, followed by as an initiator to graft PS via ATRP to afford graft copolymer PnBA-SP-PS (Figure 5D).^[88] The resultant polymers had multiple SPs in a PnBA chain. SP at a content of 0.15–0.34 wt % ($M_w = 143$ –181 kDa) afforded bright color changes as thermoplastic elastomers.

More recently, SP-diol was directly used as a co-monomer to react with bisphenol A (BPA) and triphosgene to afford SP-linked glassy polymer (Figure 5E).^[130] Because MC is a phenoxide derivative and can react with phosgene turning the MC irreversibly back to SP, a phosgene-starved approach by stepwise addition of triphosgene was employed to minimize this side reaction. The mechanism is that the MC phenoxide with para NO_2 group is less nucleophilic than BPA and SP-diol phenoxides, resulting in its reactivity the least to phosgene among the three. And the results showed that this strategy significantly prevented the undesirable reaction.

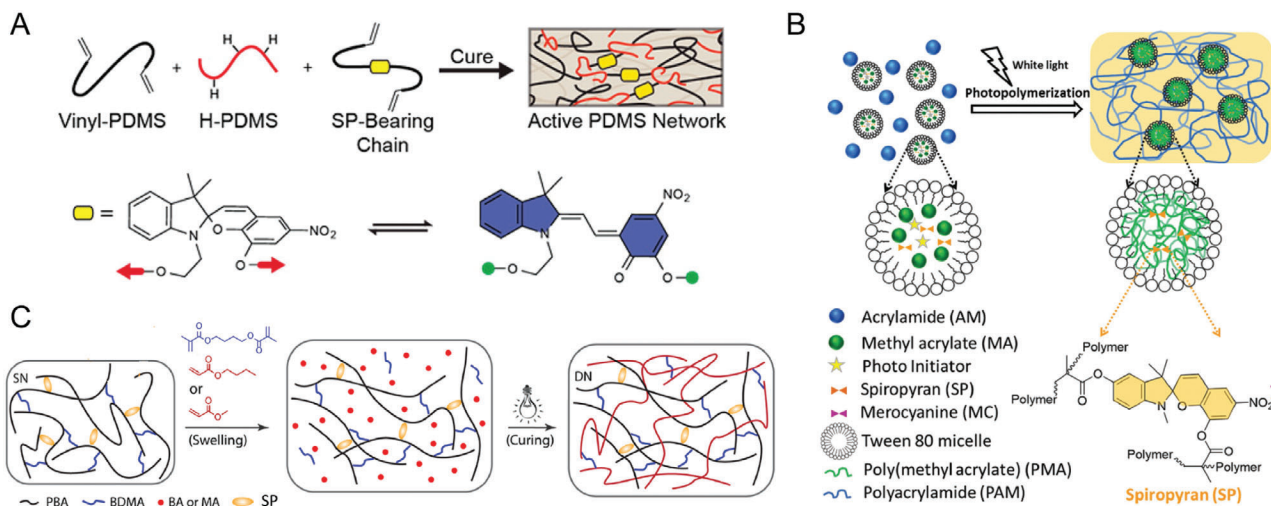


Figure 6. Synthesis of cross-linked polymers with SP as a cross-linker. A) SP-PDMS network via platinum-catalyzed hydrosilylation reaction. Reproduced with permission.^[84] Copyright 2014, American Chemical Society. B) SP-PMA cross-linked network within the micelles in hydrogels. Reproduced with permission.^[106] Copyright 2017, Wiley-VCH GmbH. C) Cross-linked SP-polyacrylates double network via photo polymerization. Reproduced with permission.^[98] Copyright 2020, American Chemical Society.

Cross-linked polymers with SPs as cross-linkers: Commercial PDMS (Sylgard 184) was used to conjugate alkene functionalized SP via a reaction of platinum-catalyzed hydrosilylation to form a cross-linked network.^[84,86,89,131–133] Vinyl-terminated SP and PDMS reacted with a hydrosilane PDMS copolymer using platinum-catalyzed thermal-curing at 65 °C (Figure 6A). Strict conditions, such as an oxygen-free environment, were not required for this reaction. The facile preparation by mixing two parts of commercial PDMS with different functionalities and SP, enables large-scale fabrication.

The functionality of bis-methylacryloyl allowed SP to be cross-linked into polyacrylates via free radical polymerization. Benzoyl peroxide was used as a radical initiator and *N,N*-dimethylaniline acted as an activator, which allowed the thermo-curing to occur at room temperature.^[43,103] Co-cross-linkers including ethylene glycol dimethacrylate (EGDMA)^[43,103–105] and poly(ethylene glycol) dimethacrylate^[103] have been used. Cross-linked SP-polyacrylates can also be prepared by free radical polymerization initiated by light. Cross-linked SP-PMA within micelles in polyacrylamide (PAAm) hydrogels were designed and synthesized via photo polymerization (Figure 6B), where a white light initiator was utilized.^[106] Following the design of multinet network elastomers,^[34] cross-linked SP-polyacrylates were synthesized and embedded within a multinet network via multiple precursor swelling-curing steps (Figure 6C).^[98]

Bis-methylacryloyl SP was also cross-linked into two commercial polyolefins, including poly(ethylene-vinyl acetate) (PEVA) and poly(ethylene-octene) (PEOC), by free radical polymerization using dicumyl peroxide as initiator under hot press.^[107] Radicals were formed on the secondary and tertiary carbon of PEVA and PEOC during the hot press processing and triggered the cross-linking between SP and the polymers. Interestingly, the SP without a nitro group was able to resist the high processing temperature (160 °C) without turning into a dark color. This preparation method of mechanochromic polymers via hot press enables a facile fabrication of mechanochromic polyolefins.

Rh, STP, and NP Synthesis: The synthesis of Rh diol (Rh-diol) included two steps starting from 2-(4-diethylamino-2-hydroxybenzyl)benzoic acid (Figure 7A), and Rh-diol reacted with hexamethylene diisocyanate (HDI), tetra(ethylene glycol) and triethanolamine via SGP to afford a linear Rh-centered PU elastomer.^[13] Rh with tri-functional groups (Rh-triol) was also reported and conjugated into a polymer matrix for mechanochromism (Figure 7B).^[14] The synthesis started from a commercially available Rh 6G, which was functionalized with hydroxyl groups followed by acrylation. The functionalized Rh was incorporated into a PEA triple-network via free radical polymerization initiated by UV light. In a more recent work, Wang et al. introduced pyrene groups into the third network of an Rh-linked PnBA triple-network.^[135] Zhang and co-workers employed the same “tri-arm” Rh and a micellar copolymerization approach to prepare Rh-linked mechanochromic hydrogels, which was similar to the strategy of synthesizing SP-linked micelle-based hydrogels shown in Figure 6B.^[136] In another work, tri-functionalized Rh was incorporated into a double network hydrogel (Figure 7C).^[137] Herein, the first-network, poly(NaAMPS-co-DMAAm) was prepared in DMSO solvent to avoid solubility issues of Rh in the aqueous phase, then the DMSO was replaced with water before fabrication of the PAAm second-network.

The Weng group designed and synthesized STP-linked polyesters (PES) and PU.^[12] The synthesis of STP-diol was similar to that of SP, with a condensation reaction between synthetic indolium and nitro thiol benzaldehyde derivatives, however, an additional hydrolysis step was required to obtain the hydroxyl groups on the benzothiopyran ring (Scheme 3A). The STP-diol was readily incorporated into PU via SGP and PES via a condensation reaction.

NP-diol was synthesized through an acid-catalyzed reaction between functionalized 2-naphthol and 1-(4-hydroxyphenyl)-1-phenylprop-2-yn-1-ol (Scheme 3B), and was then modified with vinyl groups before being cross-linked into PDMS.^[16] The functionality on the naphthalene ring was varied while that on the

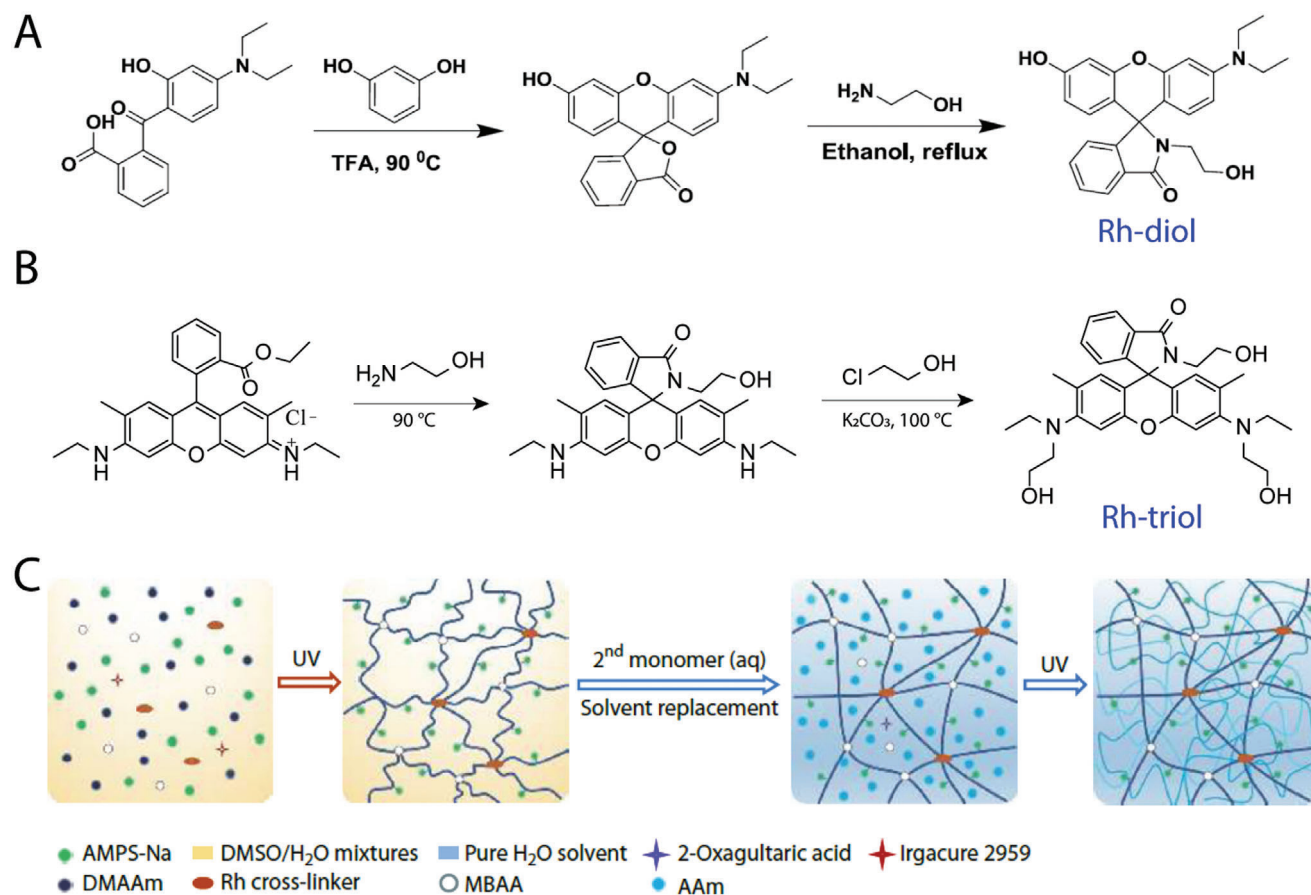


Figure 7. Synthesis of Rh and Rh-conjugated polymers. Synthetic routes for A) Rh-diol^[13] and B) Rh-triol.^[14] C) Preparation of Rh-linked DN hydrogels via free radical polymerization. Reproduced with permission.^[137] Copyright 2020, Springer Science and Business Media.

benzene ring was fixed, to afford NPs with different attachment positions.

2.2. Radical-Based Mechanochromophores

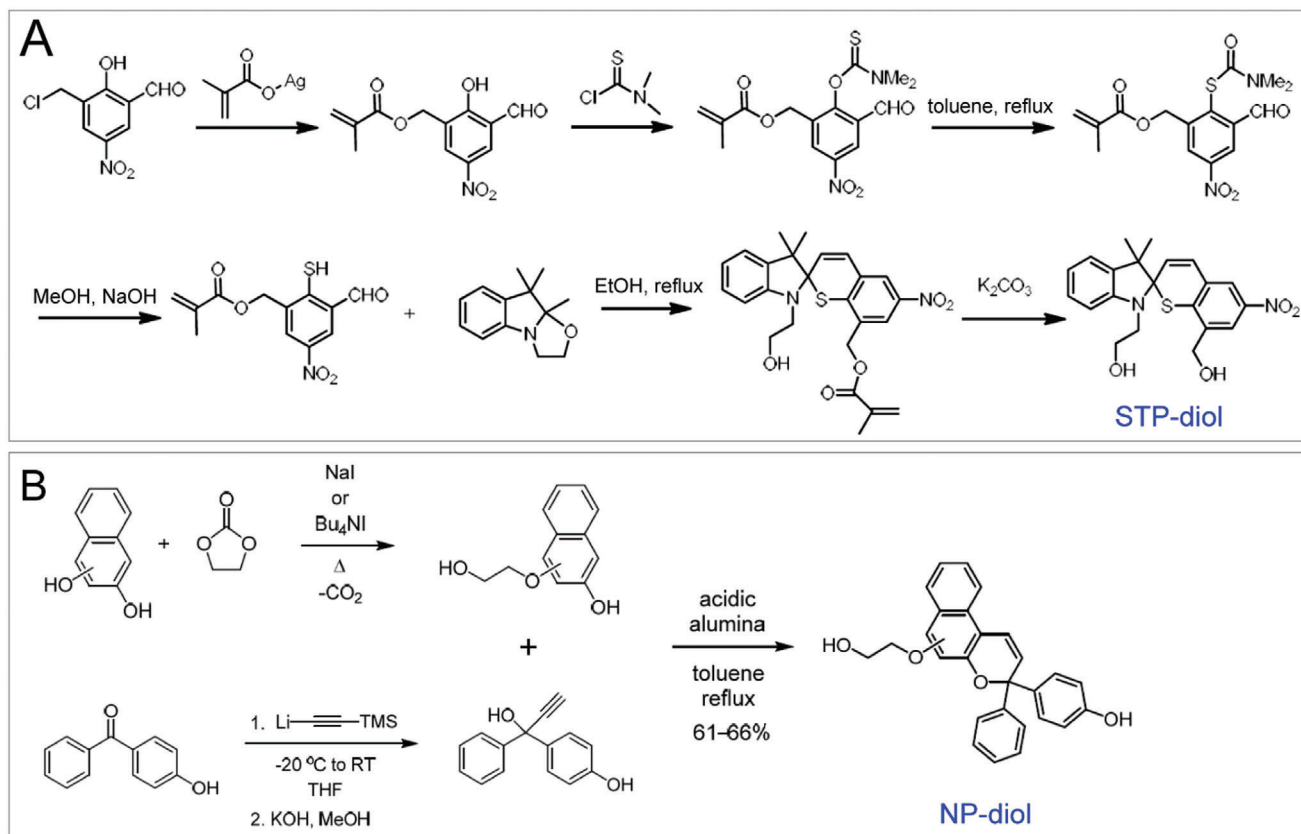
Molecules of radical-based mechanochromophores were initially introduced as antioxidants by the Scaiano group, as they found that the carbon-centered radicals on lactones, substituted nitriles or hydrocarbons, were unreactive toward oxygen (**Figure 8**).^[145–147] Dimers formed from these highly stable carbon-centered radicals via weak bonds are in thermal equilibrium with their radical precursors.^[148] This feature allows for reversible bond cleavage and recombination upon mechanical loading and unloading. Accompanied by visible color changes under force stimuli, these molecules are ideal to be used as mechanochromic force probes. Precursors to radicals were prepared before formation of dimers via a photolysis or oxidative coupling reaction.^[144,149]

Incorporation of these radical mechanochromophores into polymers has been typically achieved by reactions with hydroxyl groups. The precursor compounds for DABBF, hydroxyl terminal arylbenzofuranone, were synthesized from 4-hydroxymandelic acid and 2,4-di-tert-butylphenol, followed by modification into alkyl-hydroxyl or di-hydroxyl arylbenzofura-

none, which were then coupled to form DABBF-diol or DABBF-tetraol via photolysis under UV light using di-tert-butyl peroxide as a catalyst (**Scheme 4A**).^[17,27] DABBF-tetraol as a cross-linker and DABBF-diol as a monomer could be incorporated into PU through SGP to afford cross-linked or linear polymers.^[17,19]

In addition, DABBF-diol was modified with methoxysilane end-groups (DABBF-bis(trimethoxysilane)), which self-cross-linked into rigid silica networks through a sol-gel approach.^[19] When the DABBF-bis(trimethoxysilane) reacted with PBA terminated with methoxysilane groups, elastomeric polymer-inorganic composites were obtained, and the silica networks formed from DABBF-bis(trimethoxysilane) functioned as hard domains and the PBA chains served as soft domains (**Scheme 4B**).

Star-shaped DABBF-PS with DABBF acting as a core has also been synthesized.^[152] DABBF-diol and DABBF-tetraol were modified with 5-hexynoyl chloride to afford alkyne functionalities on DABBF. Linear DABBF-PS and four-arm star DABBF-PS polymers were synthesized by Cu-catalyzed alkyne/azide reactions between DABBF-dialkyne or DABBF-tetraalkyne and azide-terminated PS, while the eight-arm DABBF-PS was obtained by a click reaction between DABBF-tetraalkyne and in-chain azide-functionalized PS. For a further expansion of the branched architecture, DABBF-centered dendrimers were synthesized.^[150] The azide-terminated Fréchet-type dendrons in 1–4 generations, denoted by [G-*n*]-N₃, where *n* represented generation number, were



Scheme 3. Synthetic routes for STP-diol and NP-diol. A) STP-diol. Reproduced with permission.^[12] Copyright 2016, Wiley-VCH GmbH. B) NP-diol. Reproduced with permission.^[16] Copyright 2016, American Chemical Society.

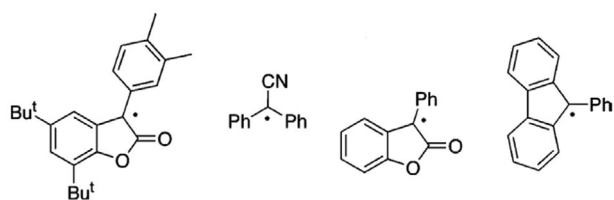


Figure 8. Chemical structures of carbon-centered radicals that are unreactive to oxygen. Reproduced with permission.^[144] Copyright 2004, American Chemical Society.

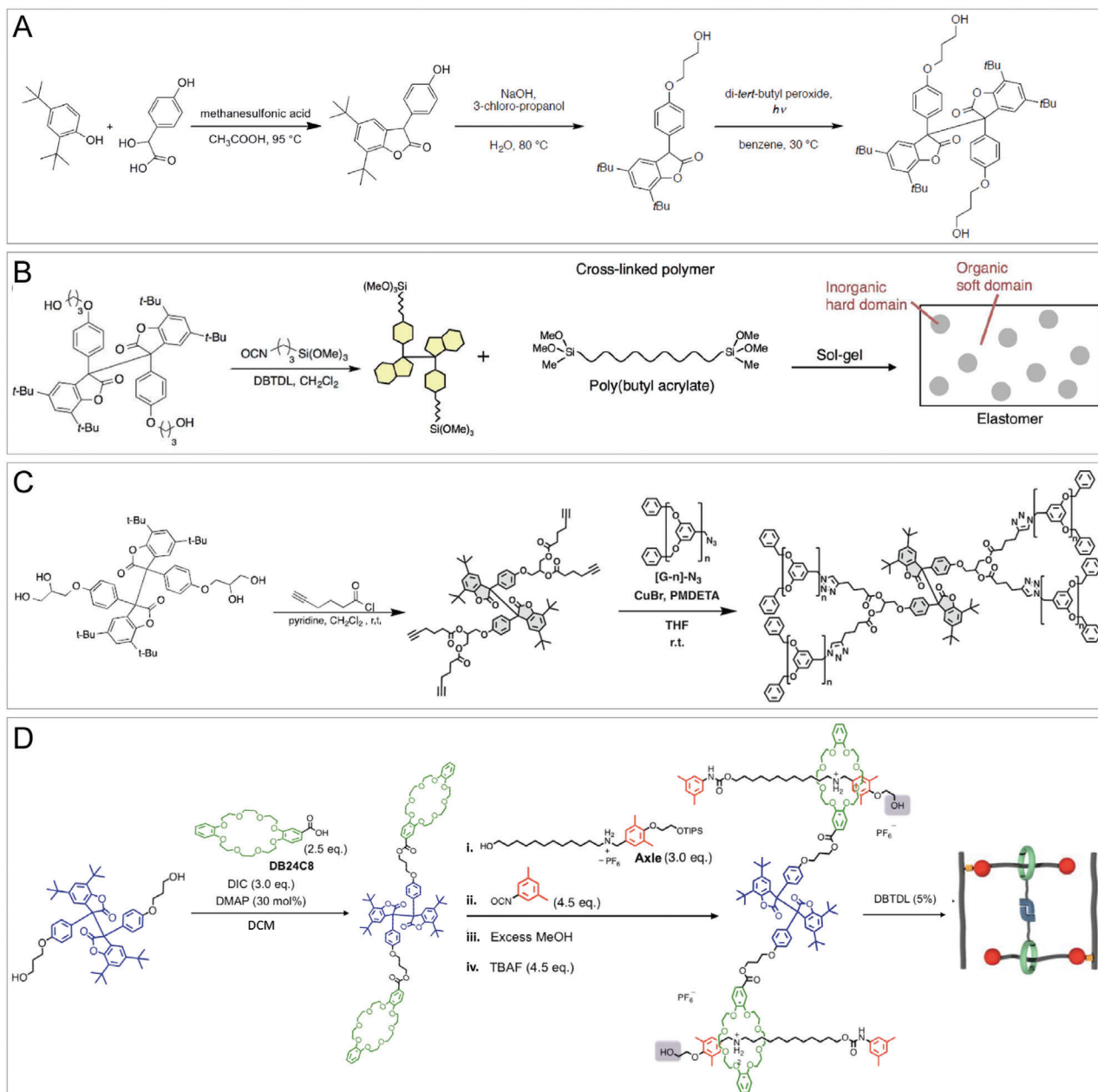
synthesized and then reacted with DABBF-dialkyne or DABBF-tetraalkyne to afford mechanochromic dendrimers (Scheme 4C). A library of DABBF-centered dendrimers varying the number of branches, combination of different dendron generations, and number of DABBF functionalities, were designed and synthesized.

Recently, DABBF was incorporated into static or sliding rotaxane cross-linking points.^[151] DABBF-diol was modified with macrocycle crown ether end groups which were then combined with axle molecules terminated with hydroxyl groups to serve as a sliding cross-linker (Scheme 4D). The sliding cross-linker was introduced into a polymer network by reacting with synthetic methyl acrylate-based copolymer containing isocyanate functionality ($M_n = 52$ kDa).

The synthesis of DABBT-diol included eight steps starting from ethyl-2-(4-methoxyphenyl)acetate, culminating in the coupling of 2-(4-(3-hydroxypropyl)phenyl)-3-hydroxythianaphthene under the catalyst of potassium ferricyanide (Scheme 5A).^[21] DABBT-diol was modified into DABBT-dialkyne through a reaction with 5-hexynoyl chloride, which reacted with azide-terminated PS to afford DABBT-linked PS via a click reaction ($M_n = 11$ kDa). In another study, four-arm star polymer DABBT-(PS-*b*-PMA)₄ was prepared using the same synthetic strategy, where DABBT was the core and PMA served as soft domains while the PS chains functioned as hard domains.^[22]

TASN-diol was synthesized in four steps (Scheme 5B) and then functionalized with alkyne groups before reacting with azide-ended PS to prepare TASN-PS polymer via the same synthetic strategy of preparing DABBT-linked PS, with $M_n = 63.8$ kDa.^[23] The modification of hydroxyl groups to di-hydroxyl was conducted before the coupling reaction for TASN-tetraol, which was used as a cross-linker to prepare TASN-PU elastomer via SGP.^[24] In addition, the same strategy of synthesizing polymer-inorganic Si-PBA/DABBF composites was used to integrate TASN into composites by modifying TASN-diol to form TASN-trimethoxysilyl which then reacted with PBA with dimethoxymethylsilyl end groups.^[153]

In a seven step synthesis, DFSN-diol was prepared by beginning from fluorene-2-carboxaldehyde (Scheme 5C).^[26] This was further functionalized with bromide groups to introduce PMMA



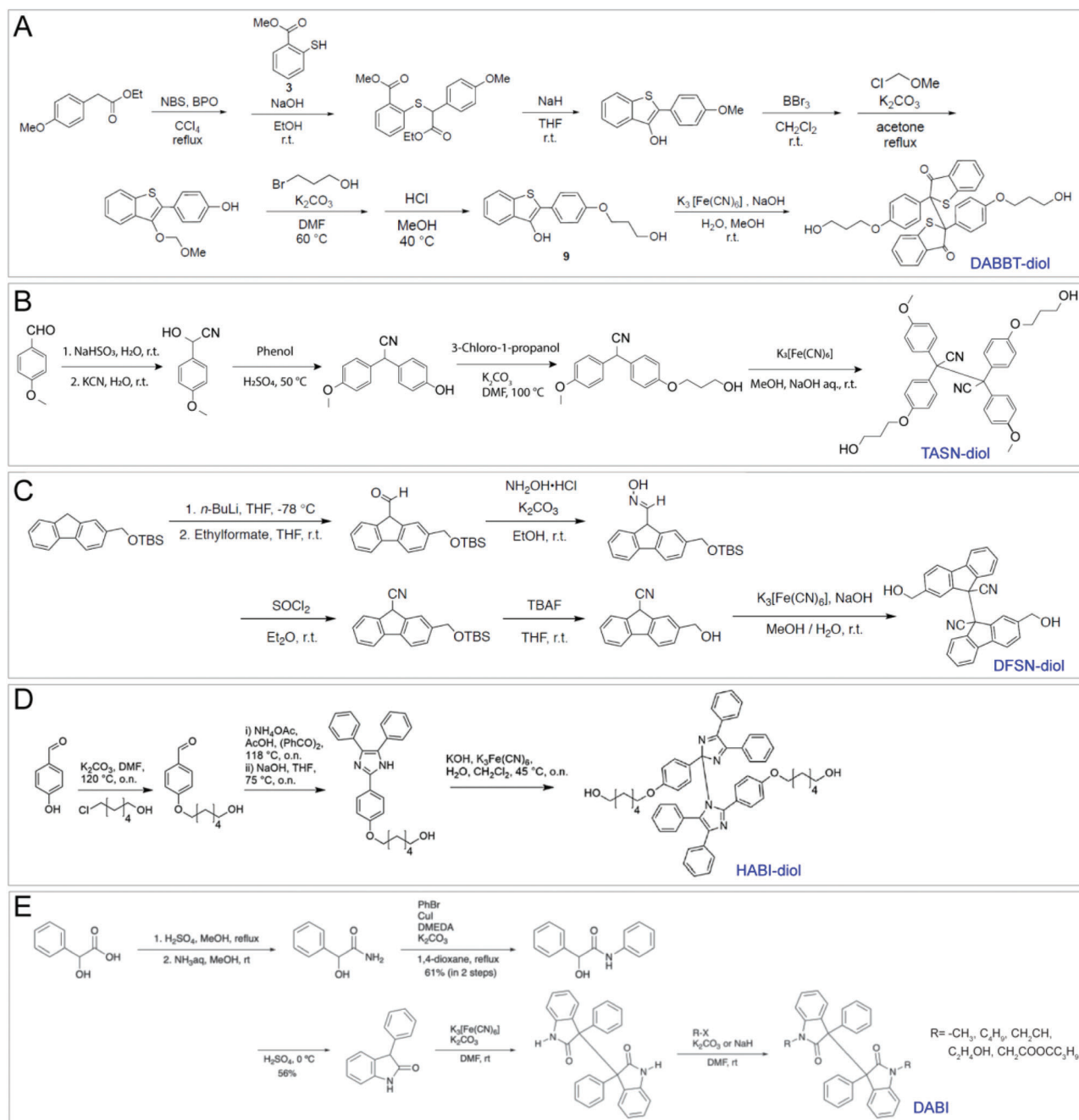
Scheme 4. Synthesis of DABBF molecule and DABBF-linked polymers. A) A synthetic route for DABBF-diol. Reproduced with permission.^[17,27] Copyright 2015, 2012, Wiley-VCH GmbH. B) Modification of DABBF-diol to DABBF-bis(trimethoxysilane) followed by incorporation into polymer-inorganic Si-PBA/DABBF composite via a sol-gel approach. Reproduced with permission.^[19] Copyright 2016, American Chemical Society. C) Modification of DABBF-tetraol to DABBF-dialkyne, which is used as a core to prepare branched polymers via a Cu-catalyzed alkyne/azide reaction. Reproduced with permission.^[150] Copyright 2019, The Royal Society of Chemistry. D) Synthesis of DABBF-rotaxane cross-linked polymer. Reproduced with permission.^[151] Copyright 2020, The Royal Society of Chemistry.

side chains ($M_n = 13$ kDa) through ATRP, affording DFSN-centered linear polymers. DFSN with bis-methylacryloyl functional groups has been cross-linked into poly(*n*-hexyl methacrylate) (PHMA) via free radical polymerization.^[154]

Four steps were required to synthesize HABI-diol (Scheme 5D).^[78] HABI-diol was readily incorporated into PU backbone, whereas the synthesis of HABI-PMA required the oxidative coupling step to be carried out after TPI was

polymerized with MA, due to an incompatibility of the dynamic equilibrium of HABI and TPI radicals under the conditions of living radical polymerization.

DABI is structurally analogous to DABBF, with the dynamic C–C bond covalently bonded to lactam instead of lactone rings.^[76] An advantage of DABI as a mechanochromophore is that the secondary amide on the lactam allows convenient substitution at the nitrogen-position. Unsubstituted DABI-H was synthesized



Scheme 5. Synthesis of radical-based mechanochromophores with hydroxyl groups. A) DABBT-diol. Reproduced with permission.^[21] Copyright 2018, John Wiley & Sons. B) TASN-diol. Reproduced with permission.^[23] Copyright 2017, The Royal Society of Chemistry. C) DFSN-diol. Reproduced with permission.^[26] Copyright 2018, American Chemical Society. D) HABI-diol. Reproduced with permission.^[78] Copyright 2016, The Royal Society of Chemistry. E) DABI with various substituents. Reproduced with permission.^[76] Copyright 2020, Wiley-VCH GmbH.

in four steps starting from mandelic acid, and a series of substituted DABI was obtained via S_N2 reactions with alkyl halides (Scheme 5E). DABI-centered PS was synthesized through an azide-alkyne click reaction.

Overall, synthetic routes for the mechanochromophores have been well-established and most of the approaches are commonly used in organic synthesis. However, multiple steps were required to afford the mechanochromophores, with lengthy synthesis and

high cost, which makes them less attractive for commercialization.

3. Sources of Mechanical Force

There are various sources of mechanical force that have been used to trigger mechano-activation. Since the molecular change

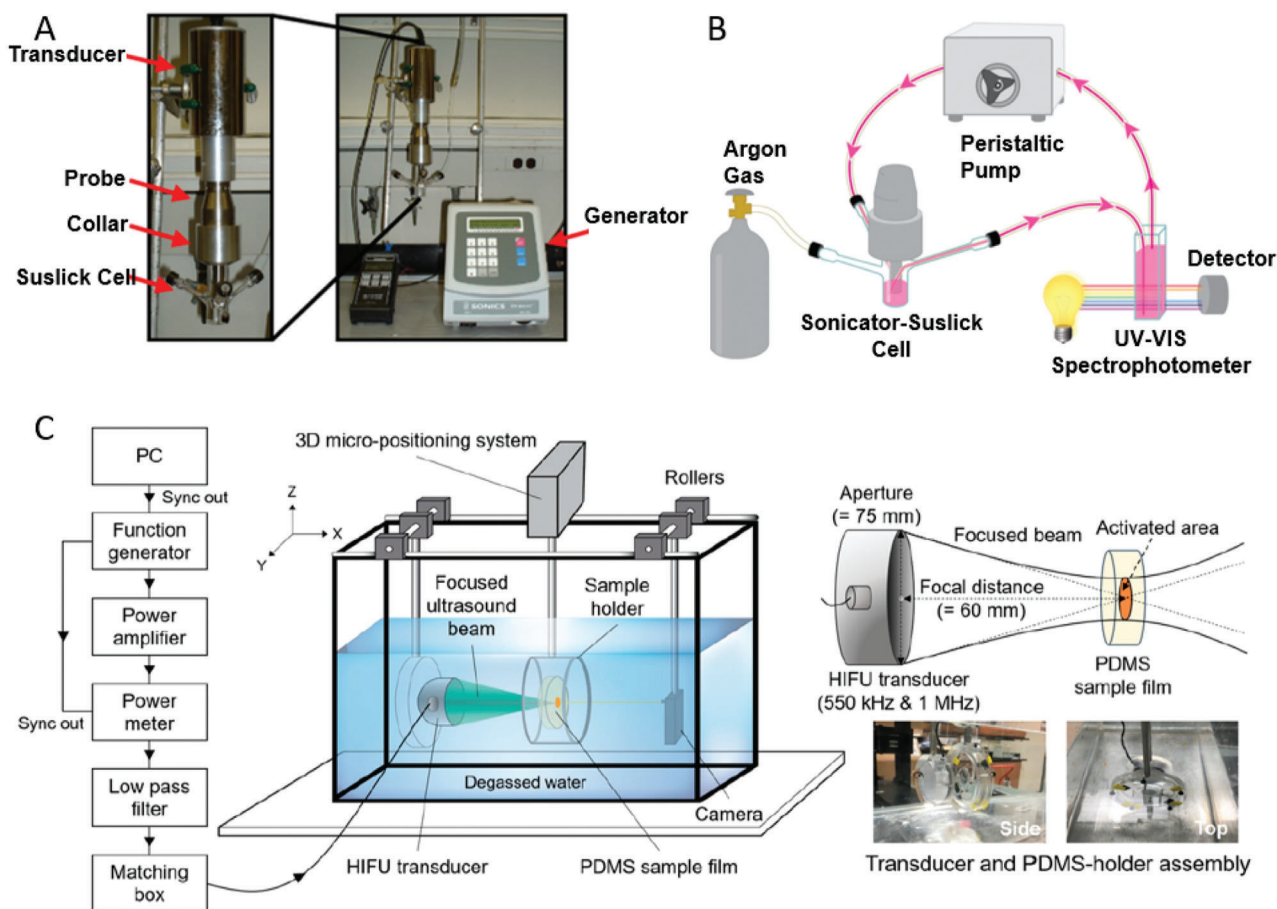


Figure 9. Setup of ultrasound apparatus for mechano-activation. A) Assembly of ultrasound equipment for mechanical activation of SP-linked PMA dissolved in solvent. Reproduced with permission.^[42] Copyright 2007, American Chemical Society. B) Schematic diagram of a flow system coupling an ultrasound equipment with a UV-vis spectrometer and a peristaltic pump for transporting polymer solution to achieve in-situ measurement. Reproduced with permission.^[113] Copyright 2016, American Chemical Society. C) Schematic diagram of sonication setup for mechanical activation of NP-linked PDMS elastomer. Reproduced with permission.^[139] Copyright 2019, United States National Academy of Sciences.

of isomerization-based mechanochromophores is accompanied by a change in visible color, absorbance, or light emission, the mechano-activation can be characterized by RGB color analysis, absorption measurements, or fluorescence imaging respectively. As radicals are generated during the activation of radical-based mechanochromophores, they are mainly measured by electron paramagnetic resonance spectroscopy (EPR), which can quantify the concentration of radicals generated from the dissociated mechanochromophores.^[20]

3.1. Ultrasound

Pulsed ultrasound has been used to turn a solution of SP-PMA (170 kDa) in acetonitrile from colorless to pink.^[42] Here a Suslick cell was used in direct contact with the solution, at a constant distance between the titanium tip and bottom of the cell (Figure 9A). The system was required to be kept cool to avoid thermo-activation of SP, induced by the heat generated from ultrasound. Different acrylic monomers were used to conjugate SP into linear chains to study the mechanochromic activation

induced by ultrasound.^[113] The ultrasound equipment was coupled with a UV-vis spectrometer equipped with a flow-cell (Figure 9B). The sample solution was transported from the Suslick cell to the spectrometer through a peristaltic pump and then returned back to the Suslick cell, to achieve in situ measurement of the SP to MC conversion and thus determine the kinetics of ultrasonic activation. A similar flow system was used to investigate ultrasonic activation of SP centered in an amphiphilic block copolymer which self-assembled into micelles.^[115] SP embedded in waterborne PU (WPU) which formed an emulsion in THF/water also displayed an ultrasonic response.^[126] P(SP-alt-F8) polymer conjugating multiple SPs in a chain (structure shown in Figure 5A) has shown mechanochromic properties triggered by pulsed ultrasound.^[91]

Mechano-activation by ultrasound was not only limited to polymer dissolved solutions but has also been applied to bulk materials. A cross-linked NP-PDMS elastomer was subjected to high-intensity focused ultrasound (HIFU) to induce the ring-opening reaction.^[139] The setup of HIFU included components for controlling the sonication pressure, location, and duration to provide a non-invasive activation approach (Figure 9C).

3.2. Tension and Compression

Coloration of a mechanochromophore-linked bulk sample has been commonly activated by uniaxial tension and compression.^[82–84] The specimens for tensile and compression testings required a relatively large amount of product, compared to ultrasound activation of dilute solutions. Although they are the most common loading modes for mechanochromic activation, they are only applicable to elastic polymers being measured at room temperature. For glassy polymers, the testing temperature was required to be elevated to increase the mobility of polymer chains to induce mechano-activation.^[82,110] On the other hand, tensile tests have been less used for radical-based mechanochromophores compared to isomerization-based mechanochromophores. One example of stretching-induced color-switching was observed for segmented DABBF-PU elastomer.^[18] Although the blue color was significant for the stretched sample, the dissociation ratio was lower than 0.1%. Another example, Si-PBA-DABBF polymer-inorganic composite, incorporated the DABBF in a rigid inorganic silica network, where the threshold of color activation was as low as 150% strain at 2.0 MPa stress.^[19] A comparison study between static and movable cross-linking points containing DABBF in PMA polymer was conducted by tensile testing (structure shown in Scheme 4D).^[151] A low dissociation ratio of TASN was observed in Si-PBA-TASN composites by stretching (0.0005% as determined by EPR).^[153] In a more recent study, TASN-centered PCL was utilized to visualize the necking phenomenon of a crystalline polymer during stretching.^[155]

With regard to the instrument set-up, load cells with various force capacities were used to apply macroscopic force to the samples and the elongation rate was precisely controlled with a movable crosshead. Stress-strain curves were then obtained to quantify the mechanical properties of the material. An optical camera installed on the instrument provided a convenient method for capturing the color change of the sample during deformation, thus the RGB color intensity values could be correlated with the mechano-responses on the stress-strain curves.^[84,87] In addition to optical image recording, in situ fluorescence imaging has been designed, which consisted of a load cell, a green diode laser for sample excitation, focusing lens, a light filter, and a charge-coupled device detector.^[110–112]

3.3. High Strain Rate Loading and Shearing

Although the commonly used tensile/compression loading methods are not ideal for mechano-activation of SP-linked glassy polymers, a high strain rate of loading provides an opportunity to study these materials. Shockwaves induced by acoustic pulses with extremely high strain rates, 1×10^7 to 10^8 s⁻¹, were applied to SP-PS samples to induce mechano-activation.^[114] The activation was captured by ex situ fluorescence imaging, and a comparison between the active SP-PS and a control sample elucidated that the force was the key for the activation rather than the generated heat. Another study employing a high compressive loading rate (1×10^2 to 10^4 s⁻¹) to activate SP-PMMA was reported by Hemmer et al.^[81] The high rate impact resulted in fragmentation of the bulk samples with a visual color around the

fractured surfaces. The high strain rate-induced optical transition enabled crack tracking for glassy polymers under extreme conditions. High strain rate compression was also employed to study its effect on activation of SP cross-linked elastomers.^[156]

The deformation caused by shearing has been shown to induce the ring-opening of SP in polymers.^[103] Here torsion testing was performed using a rheometer equipped with a fluorescence imaging set-up. Coloration and fluorescence were generated after the bulk polymer yielded under shear. Shear-induced activation of the specimens with longer primary co-cross-linkers required lower activation stress but a larger strain under a higher shear rate (0.1 rad s⁻¹).

In terms of versatility, the apparatuses of force loading equipped with fluorescence imaging components are limited in a few research groups. Easy-to-establish and reliable testing approaches are necessary for expanding the development of this field. In such case, in situ optical photo capturing is more convenient, making the mechanochromophores with visible color changes more attractive for practical use.

3.4. Swelling

As another type of loading methods, the deformation generated from polymer swelling has been proved sufficient to activate mechanophore cross-linked in polymer matrices. The Moore group proved this concept on SP cross-linked PMMA (Figure 10A).^[157] Different organic solvents were used to swell SP-PMMA to show the influence of swelling speed on the mechanochromic performance. The solvents with moderate polarity could efficiently induce the mechanochromic activation with a significant color change, whereas neither highly polar solvents nor apolar solvents could induce a significant color change because of a limited swelling ratio or a slow swelling rate. Although an extremely fast swelling speed in chloroform could effectively cause the color change, the specimen fragmented. The color intensity was directly correlated to swelling ratio, verified by removing cross-link density. Reversibility of the color change by removal of the solvents was not mentioned.

Alternatively, microgels of SP cross-linked with monomer 2-(diethylamino)ethyl-methacrylate (DEA) showed swelling induced mechano-activation when treated with CO₂ gas (Figure 10B).^[158] The microgels swelled due to protonation of the tertiary amine groups on PDEA under CO₂ treatment, resulting in a transition from water non-swelling to water-swelling microgels. The color change was reversible, and deprotonation of the amine groups by purging with N₂ gas led to deswelling of the microgels, resulting in the color fading. Studies reporting mechanochromophore activation by the force from solvent swelling are still rare and their potential for practical applications remains to be explored.

3.5. Grinding

Grinding is the most common source of mechanical force that has been used to study the radical-based mechanochromophores and their covalently linked polymers in powder state.^[19,21,23,26,76,152] Normally a milling machine was used, where

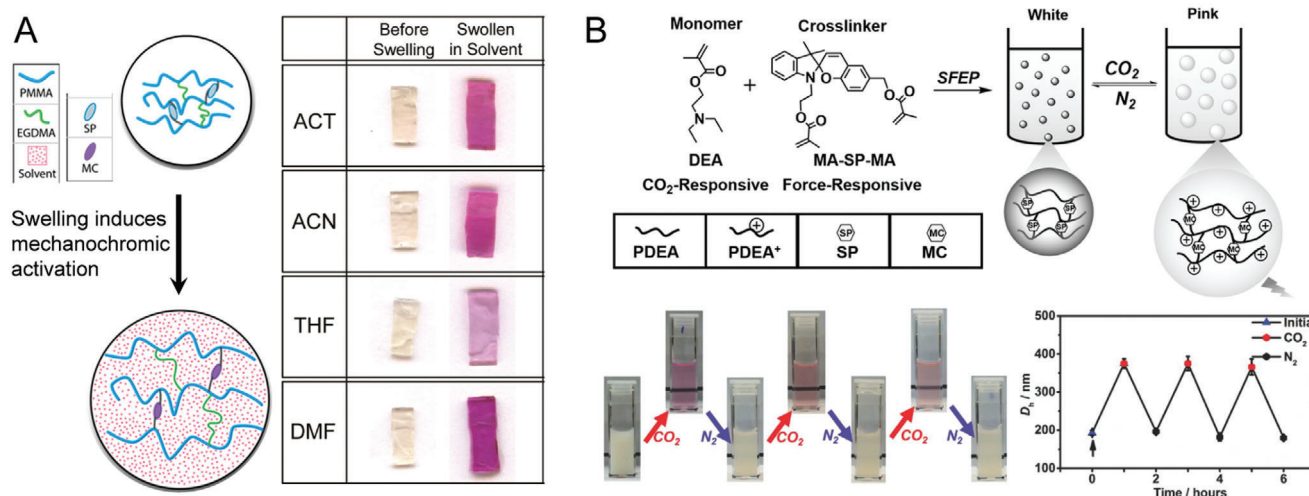


Figure 10. Swelling-induced color activation of SP-linked polymers. A) Schematic illustration and optical images of SP cross-linked PMMA before and after swelling in organic solvents: acetone (ACT), acetonitrile (ACN), tetrahydrofuran (THF), and dimethylformamide (DMF). Reproduced with permission.^[157] Copyright 2014, American Chemical Society. B) SP cross-linked PDEA microgels swelling in water by purged with CO₂. Optical images of the color change by alternatively purging with CO₂ and N₂, and DLS data of the size change of the microgels. Reproduced with permission.^[158] Copyright 2016, Wiley-VCH GmbH.

the grinding speed can be controlled. Grinding the powder in a mortar has also been used but the grinding speed cannot be controlled.

The radical form of diarylacetonitrile (DAAN) exhibits a pink color and a yellow fluorescence when generated from TASN cleavage. Recently, DAAN has been employed as a molecular probe to visualize polymeric mechanically-generated radicals in bulk materials, produced from the scission of polymer chains. Upon grinding, the mixture of DAAN and PS,^[159] or DAAN conjugated PS^[160] generated a yellow fluorescence and a pink color due to the mechanically-generated radicals transferred to DAAN, enabling a visualization of polymer chain scission.

3.6. Freezing

The mechanical force generated from solvent freezing was utilized to trigger the dissociation of radical-based mechanochromophores. Cross-linked DABBF-PU swollen with 1,4-dioxane changed color upon freezing, with the onset temperature of 4 °C which was close to the freezing point of 1,4-dioxane (12 °C), as shown in **Figure 11A**.^[17] Cross-linked TASN-PU was shaped into cubes via solvent casting and swollen with 1,4-dioxane, and the yellow gel turned pink when frozen in liquid nitrogen, while emitting yellow light under UV (**Figure 11B**).^[24] The freezing-induced mechanochromism was solvent affinity dependent, and was only applicable to solvents with a high melting point and a high swelling degree. The force from freezing was also demonstrated on ring-opening mechanochromophore Rh.^[137]

3.7. Crystallization

The force generated during crystallization has been reported for inducing mechanochromic activation.^[161] In the design, PCL

was utilized to conjugate a radical-based mechanochromophore, TASN, owing to the relatively low melting point and crystallization temperature of PCL. During the isothermal crystallization via a melting-cooling process, both TASN-centered linear PCL and TASN-cored star PCL turned pink, suggesting bond cleavage occurring to TASN. The micro-mechanical force generated from polymer crystallization not only enabled an efficient mechanochromic activation, but also provided more options of mechanical stimuli for smart materials.

4. Factors Influencing Mechano-Responses

Computational simulations have been used to study the selective breakage of weak bonds on mechanochromophores, including first-principles steered molecular dynamic and constrained geometries simulate external force (COGEF) at density functional theory (DFT) level.^[43] The attaching points on SP were pulled in opposite directions while calculating the distance of C–O and their relative energy. COGEF simulation was also employed to calculate the energy of C–N rupture for difunctionalized Rh.^[13] On the macroscopic level, any aspects that influence energy transfer to mechanochromophores and force distribution will affect the mechanochromic responses, which becomes more complicated when polymer matrices are involved. To improve the efficiency of mechanochromic function, it is important to understand the influencing factors.

4.1. Geometry and Substituent Effects

As the mechano-activation requires both moieties on the weak bond in a mechanochromophore to be connected to polymer chains for force transmission, the covalently linked positions on the mechanochromophore are vital. The Craig group adopted

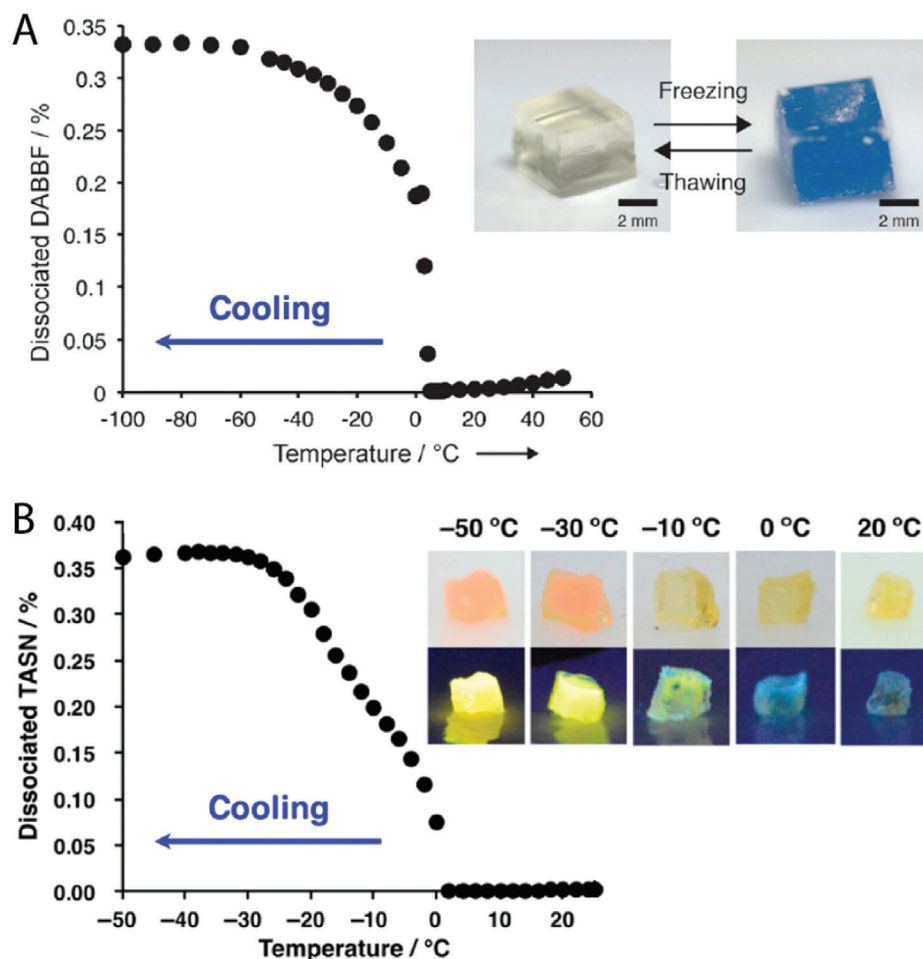


Figure 11. Freezing-induced dissociation of radical-based mechanochromophore-linked polymers. A) Optical images of cross-linked DABBF-PU swollen with 1,4-dioxane before and after frozen in liquid nitrogen, and percentage of the dissociated DABBF in the gel during freezing. Reproduced with permission.^[17] Copyright 2015, Wiley-VCH GmbH. B) Images of TASN-PU swollen in 1,4-dioxane under room light and UV light irradiation, and plot of dissociation ratio against temperature during the cooling process. Reproduced with permission.^[24] Copyright 2018, American Chemical Society.

a single-molecule force spectroscopy (SMFS) to investigate the ring-opening energy of two 6-nitro-SPs with different linkage positions on the indoline ring ($SP_{5,8}$ and $SP_{1,8}$).^[118] SP-linked copolymers were synthesized via ring opening metathesis polymerization (ROMP) with a cyclooctadiene monomer (9-oxabicyclo[6.1.0]non-4-ene), which could increase their adhesion with the AFM tip. A single SP-linked copolymer chain was pulled by an AFM tip, and the results revealed that $SP_{1,8}$ (SP2 in Figure 12A) required less force and a shorter extension for bond breakage than $SP_{5,8}$ (SP1). This study provided insights into the geometry effect on the mechanochromism on a molecular level. The macroscopic response of these two SPs conjugated in PDMS was also investigated.^[86,162] Compared to the computational calculations which showed that $SP_{1,8}$ was more advantageous at the mechano-response over $SP_{5,8}$, Kim et al. reported that the mechanochromic reactivity (onset stress/strain and fluorescence intensity at a specific strain) of these two SP-PDMS systems were indistinguishable.^[162] However in our study, although the onset strains of the two SPs in PDMS were almost identical, the color intensities at a specific strain were different.^[86]

In another work, the geometry effect on mechanochromism was investigated via varying the attachment positions on the benzopyran moiety (SP (p), SP (m), and SP (o)) (Figure 12B).^[133] The three SPs without nitro groups were covalently incorporated into PDMS. Uniaxial tensile testing demonstrated that the order of the colorimetric intensity response was SP (o) > SP (m) > SP (p) but the onset of color activation identically occurred at around 90% strain. The results of COGEF modeling indicated that the mechanical response was dependent on the contour length of the stretched polymer chain, with a greater contour length leading to a greater mechanochromic response.

SP without a nitro substituent at the 6-position is UV inactive^[87,116] and undergoes a faster backward reaction from MC to SP^[164,165] due to the absence of a strong electron-withdrawing group. SP (o) substituted with H, Br, or NO_2 at the 6-position were used to study the effect of substituents on mechano-reactivity (Figure 12C). The force-extension curves revealed that the trend of critical force for C–O rupture relative to the substituent was $H > Br > NO_2$, which was consistent with a theoretical study^[166] reporting that an electron withdrawing

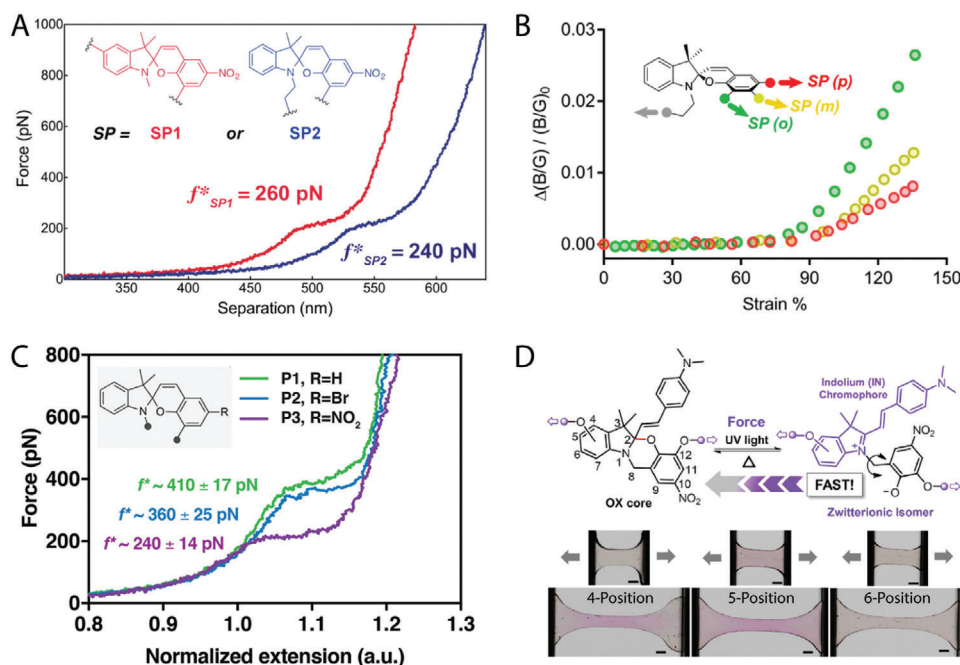


Figure 12. Study of geometry and substituent effects for isomerization-based mechanochromophores on mechano-activation. A) Force-separation curves of two SPs varying attachment positions on the indoline part, measured by SMFS. Reproduced with permission.^[118] Copyright 2015, American Chemical Society. B) Plot of blue/green color intensity ratio against strain for three SP-PDMS samples varying attachment positions on the benzopyran side. Reproduced with permission.^[133] Copyright 2018, American Chemical Society. C) Force–extension curves of three SPs with different substituents at 6-position, measured by SMFS. Reproduced with permission.^[89] Copyright 2018, American Chemical Society. D) Structures of an oxazine-based mechanochromophore and images of three regioisomers linked in PDMS before and under strained. Reproduced with permission.^[163] Copyright 2021, Cell Press.

group on the para position to O atom can enhance the conversion of SP to MC, due to a stabilization of the negative charge at the O atom. The speed of forward conversion from SP to MC showed an opposite trend to the backward reaction from MC to SP, meaning that the factor stabilizing MC is more advantageous for the forward conversion and unfavorable for the backward transformation. More recently, a new mechanochromophore based on 1,3-oxazine was reported for a fast color-fading rate (Figure 12D).^[163] Three regioisomers with varying attachment positions on the indole ring were covalently linked in PDMS, and the one attached at the 5-position presented the most obvious color change among them. This is because the electron-donating para-substituent can stabilize the ring-open isomer.

Rh-linked polymers with two or three attachment sites on Rh have been reported to have different mechanochromic performances. When Rh-PU first showed mechanochromism, an Rh molecule with two attachment positions was designed (Figure 13A) and the polymer underwent a single color transition under loading.^[13] Later, Wang et al. reported Rh-linked polyacrylates with three attachment positions (Figure 13B).^[14] The elastomers went through three fluorescent colors, blue, pink, and yellow corresponding to before, under, and after stretching, respectively (Figure 13C). DFT calculation demonstrated that a twisted ring-closed structure turned into a planarized ring-open zwitterion under stretching, and relaxed to a bent zwitterion upon external force removal, which can explain the occurrence of a new emission band at 600 nm for the elastomers when stretched and then a blue-shift to 550 nm after relaxation, corresponding to the

three fluorescent colors (Figure 13D). The blue shift of absorption under and after stretching was 28 nm, but the difference between the two visible colors was not significant to the naked eye. For the difunctional Rh-based elastomer, a smaller redshift upon stretching was observed, indicating that the planarization was not as sufficient as the tri-functional Rh.

The regiochemical effect for NP was investigated by Robb and co-workers.^[16] The attachment positions on NP were varied, as denoted by NP5, NP8, and NP9 (Figure 14A). DFT calculations based on COGEF showed that the force of C–O cleavage for NP5 was significantly lower than that for NP8 and NP9. When the NP-PDMS elastomers were stretched, only the NP5 underwent a color switch from colorless to orange-yellow, whereas neither NP8, NP9 nor the control (mono-functionalized NP) displayed a color change. This could be explained by a lower estimated energy of the C–O breakage as well as a smaller angle of the orientation between the applied force and the C–O bond for NP5. In terms of substituent effect, NPs were modified with an electron-donating pyrrolidine at the para position on the phenyl ring which was not connected to polymer chains, an ortho-fluoro group on one of the phenyl rings, or an alkyl tether substituent at the 5-position, before they were cross-linked into PDMS (Figure 14B).^[140] Due to a strong electron-donating capacity, a red shift was observable for the NP with a pyrrolidine group when activated to MC under force or UV irradiation, displaying a purple color instead of orange-yellow. The fluoro group on the aromatic rings allowed the color fading to slow down because of steric hindrance, whereas replacement of the electron-donating

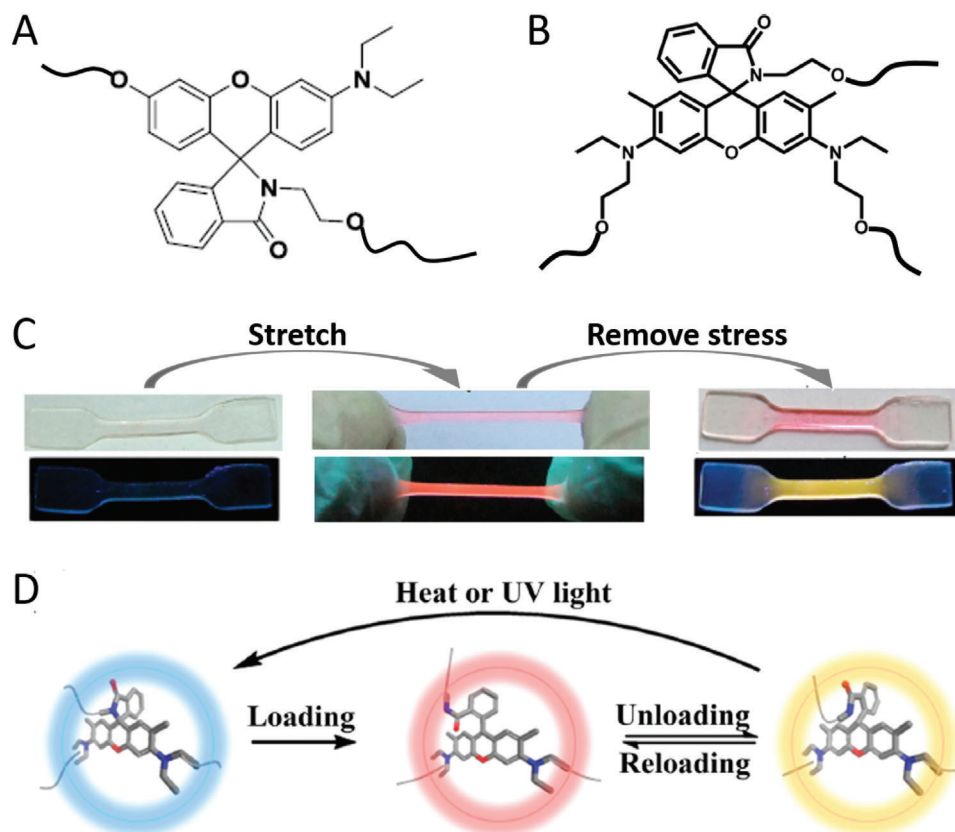


Figure 13. Mechanochromism of Rh-linked polymers varying attachment positions. A) Chemical structure of “two-arm” Rh-polymer. Reproduced with permission.^[13] Copyright 2015, Wiley-VCH GmbH. B) Chemical structure of “tri-arm” Rh-polymer. C) Pictures of fluorescent and visible color changes for “three-arm” Rh-linked polyacrylate elastomer before, under and after stretching. D) Illustration of molecular geometries of Rh induced by force resulting in a transition of three fluorescent colors. Reproduced with permission.^[14] Copyright 2017, American Chemical Society.

alkoxy group with an alkyl tether on NP sped up the color fading. The tunable mechanochromic properties can be useful for designing multi-color switching materials.

DABIs substituted with different functional groups at the N-position were ground to compare their mechanochromic responses (Scheme 5E).^[76] The unsubstituted DABI-H exhibited the highest dissociation ratio compared to the other substituted DABIs, which was attributed to intermolecular hydrogen bonds among DABI-H molecules, enhancing the efficiency of force transmission. In another example, TASN with diarylurea substituents exhibited much higher mechano-activation in response to grinding than those substituted with hydroxyl, methoxy, or nitro groups, benefiting from the hydrogen bonding formation.^[167] However, these investigations regarding the substituent effect on radical-based mechanochromophores were only demonstrated for small molecules without conjugation into polymer matrices.

4.2. Polymer Architecture

In the discussion above, the geometry and substituent effects on the mechanochromic properties only focus on the structure of mechanochromophores. The effect of polymer architecture is more complicated and can be used to provide further strategies to govern mechanochromic performance.

4.2.1. Position of Mechanochromophores in Polymer Matrices

Stress usually tends to accumulate in or near the middle of polymer chains to induce degradation.^[168,169] A dimer-based mechanophore, coumarin, was incorporated into PMA backbone either centered or off-centered, and it showed that only the chains with centered mechanophores underwent a sufficient dimer dissociation when sonicated, whereas the chains with off-centered mechanophores preferred non-specific random scission.^[170] Based on this principle, mechanochromic polymers normally included centered mechanochromophores in the backbone, unless multiple mechanochromophores were incorporated. Ultrasound activation of SP-centered PnBA was shown to be polymer chain length-dependent.^[85] When the repeating unit nBA on each side of SP was lower than 10, the color change was not distinguishable. For the repeating unit higher than 30, the chain was too long to induce a bright color, due to an inefficient force transmission to the SP. Another study showed that the mechanochromic performance was mainly determined by the degree of polymerization rather than the molecular weight or the type of side chains.^[113] In a linear DABBF-PU system, an increase in the molecular weight led to an increase in the DABBF dissociation ratio upon grinding.^[152]

Mechanochromophores centered in polymer chains can be regarded as a core connecting to two polymer arms, and

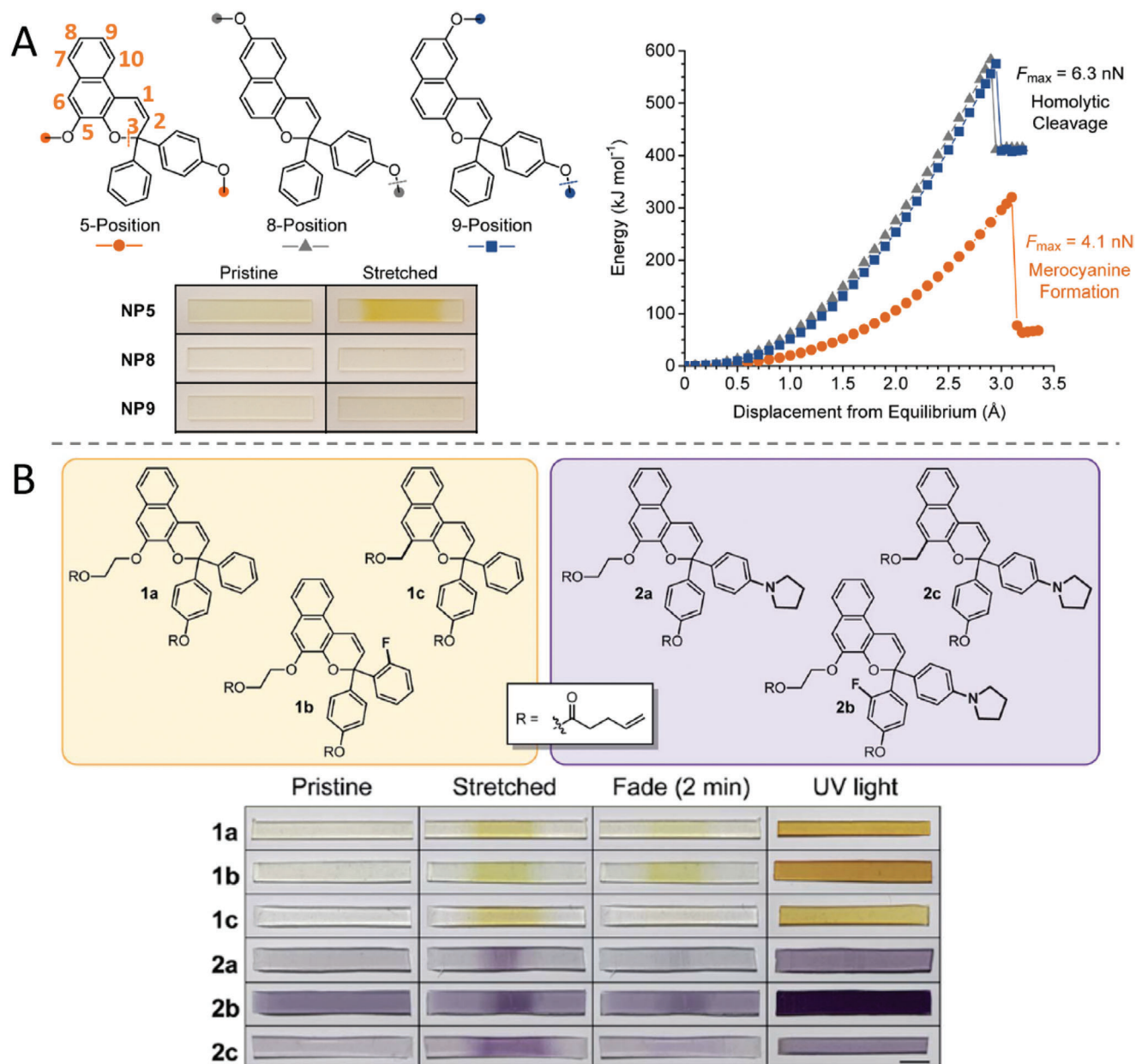


Figure 14. Regiochemical and substituent effects on mechanochromism for NP. A) DFT calculations for three NPs varying attachment positions on their mechano-responsiveness, and images of the corresponding PDMS elastomers before and after stretched. Reproduced with permission.^[16] Copyright 2016, American Chemical Society. B) Chemical structures of NP with different substituents and images of the NP cross-linked PDMS elastomers under different stimuli and conditions. Reproduced with permission.^[140] Copyright 2020, The Royal Society of Chemistry.

there are some mechanochromophore-polymers that have their mechanochromic core covalently linked to multiple polymer chains. A tetrafunctional rigid Si-DABBF network formed from DABBF-tetraol showed a higher dissociation ratio (14%) than the network synthesized from difunctional DABBF-diol (7.6%).^[19] Linear, four-arm, and eight-arm DABBF-PS were activated by grinding, and the ratio of dissociated DABBF increased with increasing arm number when comparing these polymers with a similar molecular weight (**Figure 15A**).^[152] For the DABBF-centered dendrimers, activated by ball milling, increasing the number of branches led to a higher ratio of DABBF cleavage

(Figure 15B).^[150] It was concluded that an improved force transmission and an enhanced suppression of recombination of radicals was afforded by increasing dendrimer generations and dendron units, to increase the mechanophore dissociation. It was also found that the DABBF-cored dendrimers with various functionalities displayed mechano-activation at different levels, with a higher DABBF cleavage ratio for the dendrons with more polar end groups.^[171] This was because strong intermolecular interactions were provided by the multiple terminal polar functional groups so that they could reduce the chain mobility thus enhancing the force transmission to the mechanophores

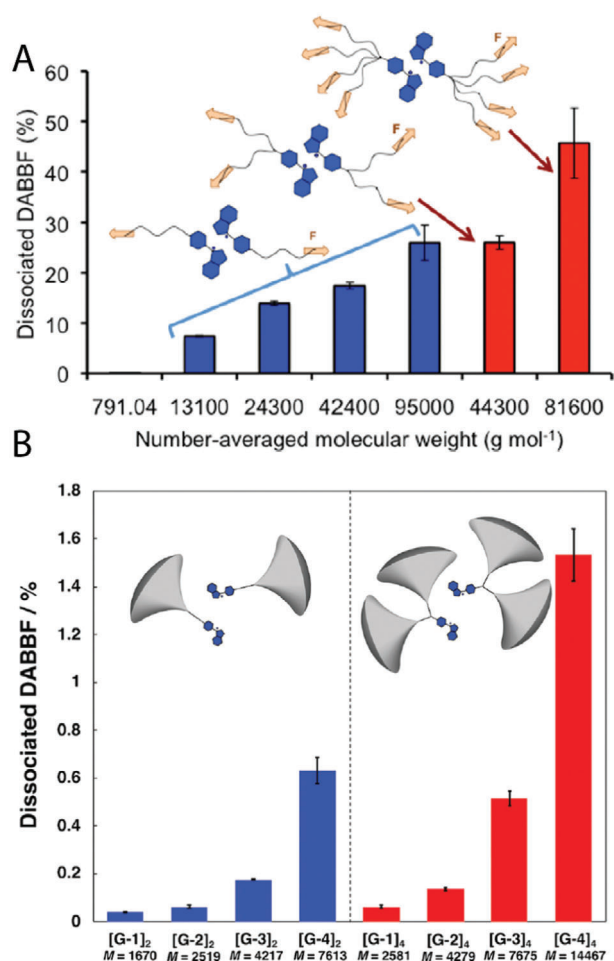


Figure 15. Branched polymers with DABBF as the core. A) Ratio of dissociated DABBF in the samples of pure DABBF-diol, linear, four-arm and eight-arm star DABBF-linked PS. Reproduced with permission.^[152] Copyright 2016, American Chemical Society. B) Ratio of DABBF cleavage in dendrimers with different generations. Reproduced with permission.^[150] Copyright 2019, The Royal Society of Chemistry.

and suppressing the recombination of the generated radicals.

From the examples above, varying the location of mechanochromophores in polymers has an effect on the mobility of polymer chains, which results in a change in mechanochromic performance. SP located in the hard segment exhibited a higher mechanical activation than SP located in the soft segment for the PU with a high content of hard segment (40 wt %), but a similar level of activation was observed for the both SP locations for the PU with a relatively low hard segment content (22 wt %).^[120] This was due to a more significant segregation of soft and hard segments in the high hard segmental systems resulting in inhomogeneous force distribution, despite less alignment of SP, caused by a lower mobility. This suggests that a certain level of mobility for polymer chains can effectively promote mechanochromic activation. For glassy SP-PMMA, color activation was strongly dependent on polymer mobility, as the activation occurred at a temperature range of 90–105 °C under a specific strain rate.^[110] When SP-PMMA

was plasticized with methanol improving the stretchability, the mechano-activation was observed at room temperature. Nanofiller-like POSS was employed to hinder the mobility of the hard domains via aggregation to improve the strength of SP-PU.^[128] POSS is comparable to nanofillers such as clay, such that their addition can improve the mechanical properties of polymers. In addition, due to their chemically functionalized structure, they can be covalently linked into polymer systems without compatibility issues.^[172] Due to the cage-like structure of POSS, which forms aggregates, its introduction can significantly restrict the mobility of polymer chains.^[173,174] Thus POSS was introduced into SP-linked PU elastomer as chain extenders and cross-linkers to restrict the chain mobility to enhance the mechanochromic performance.^[128]

Examples of mechanochromophores connecting to different blocks in copolymers showed the importance of polymer chain mobility to mechano-activation. The mechano-response of tri-block copolymers PS-*Pn*BA-SP-*Pn*BA-PS was shown to be dependent on PS block length, which affected the mobility of polymer chains near SPs.^[85] A high PS hard-block fraction (PS₉-*Pn*BA₁₅-SP-*Pn*BA₁₅-PS₉) resulted in a more glassy-like polymer with a low yield strain and a high Young's modulus, leading to an insufficient mechanochromic response prior to specimen rupture. Inadequate force transferred to SP also occurred in samples with a low hard-block fraction (PS₃-*Pn*BA₁₅-SP-*Pn*BA₁₅-PS₃ and PS₄-*Pn*BA₁₉-SP-*Pn*BA₁₉-PS₄) as the specimens were too soft to transfer the applied force. This highlighted that a balance of microphase structure, enabled by hard and soft blocks leading to a desirable level of polymer mobility, was required for optimal mechanochromic activation. Graft copolymers of PBA-SP-PS with SP located between the incompatible soft and hard domains have been reported.^[88] This design reduced the possible slipping of chain entanglements under loading as the dispersed PS hard domains performed like physical cross-links with stress concentrated at the interface of PS domains, while the soft domains still provided sufficient mobility for SP isomerization. A low onset of mechano-activation was achieved at 54% strain. The mechanical and mechanochromic properties were adjustable by varying the composition of soft/hard blocks.

Reducing the polymer chain mobility has also been used to adjust the mechanochromic activation of radical-based mechanochromophores. For segmented PU with DABBF located in the soft segments, the aggregation of hard domains formed by hydrogen bonding was believed to promote the transmission of force to mechanochromophores to induce molecular dissociation under stretching.^[18] However, a comparison to DABBF located in the hard domains was not mentioned. Another system, which conjugated DABBF into a rigid silica network, also showed the importance of restricting chain mobility and recombination of the colored radicals to mechano-response.^[19] The Si-DABBF network presented a higher dissociation ratio (7.6%) than the DABBF-diol (0.14%) upon grinding. An increase in the Si-DABBF content in a Si-DABBF-PBA polymer-inorganic composite improved the toughness (Figure 16A) and resulted in a deeper blue color (Figure 16B). This was due to the majority of the DABBF dissociation occurring at the interfaces between the inorganic silica and polymeric PBA domains (Figure 16C), with a higher content of rigid silica domains slowing down the recombination of the colored radicals. This interfacial force-localizing

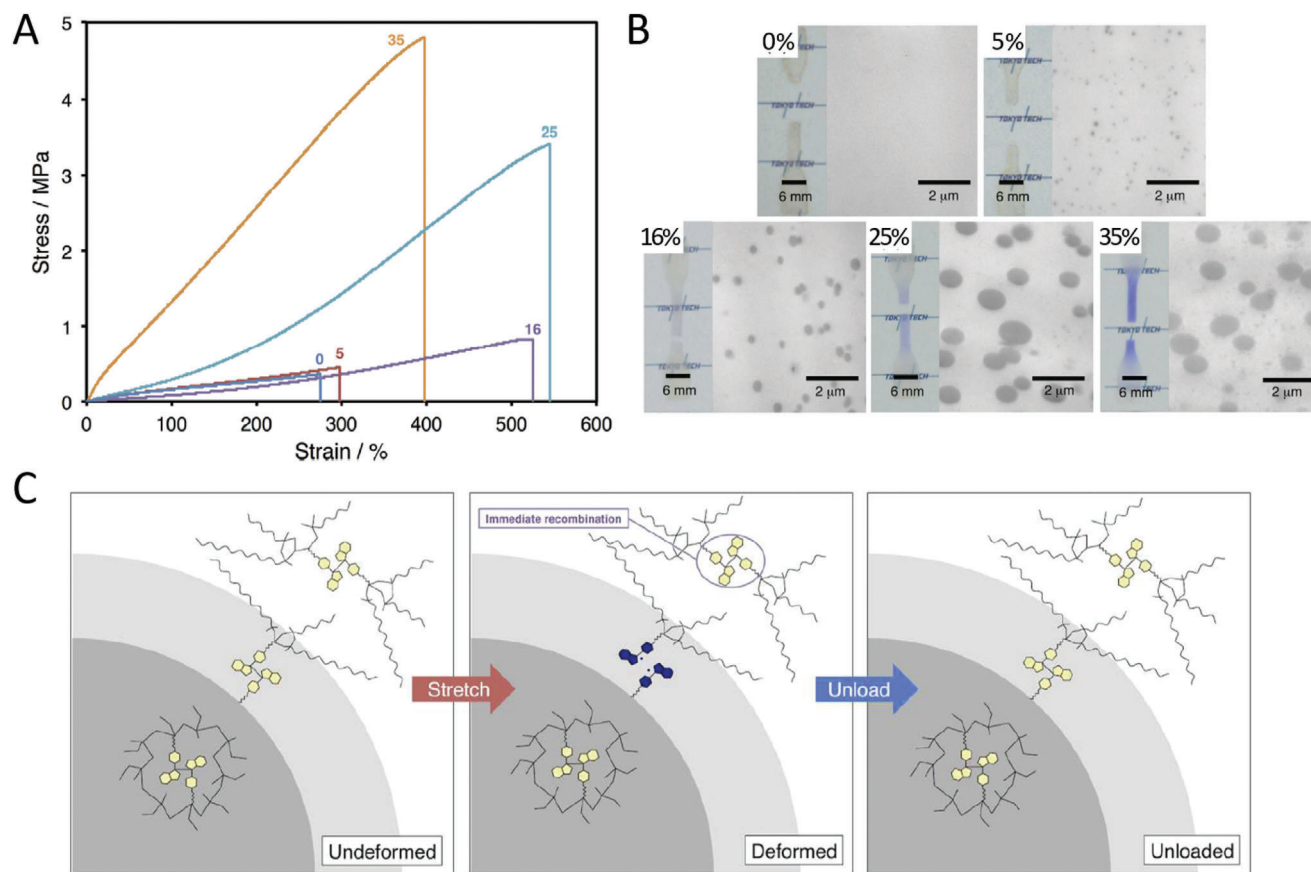


Figure 16. Enhanced mechanical properties and dissociation ratio of DABBF by introducing rigid domains in Si-PBA-DABBF polymer-inorganic composite. A) Stress–strain curves of Si-PBA-DABBF with different Si-DABBF contents. B) Images and TEM pictures of Si-PBA-DABBF with different Si-DABBF contents. C) Illustration of DABBF dissociation at the interfaces. Reproduced with permission.^[19] Copyright 2016, American Chemical Society.

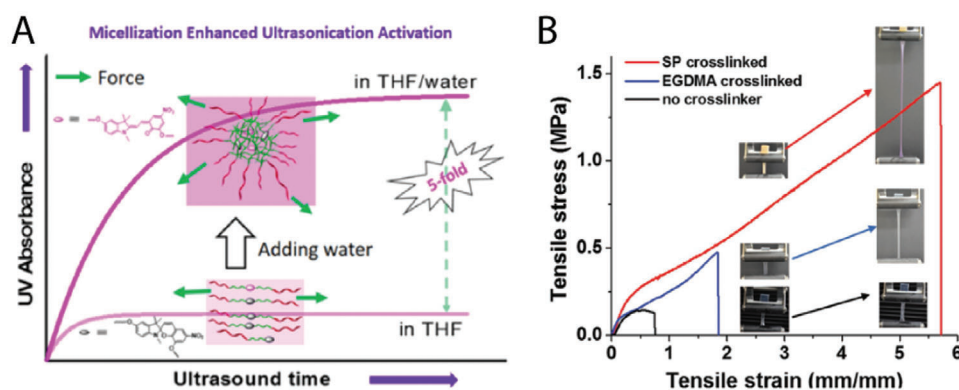


Figure 17. Mechano-responses enhanced by micellization. A) Ultrasound activation of PNIPAM-PtBA-SP-PtBA-PNIPAM micelles in THF/water or dissolved in THF. Reproduced with permission.^[115] Copyright 2015, American Chemical Society. B) Tensile stress–strain curves of hydrogels using SP or EGDMA as cross-linkers or without cross-linkers. Reproduced with permission.^[106] Copyright 2017, Wiley-VCH GmbH.

strategy was also applied to SP-containing systems^[175] and further expanded to incorporate two different mechanochromophores, DABBF and NP, to achieve multi-color switching.^[141]

Several research groups have designed mechanochromophores within micelles to enhance mechanochromic performance. When SP was embedded in the center of an

amphiphilic polymer chain (PNIPAM-PtBA-SP-PtBA-PNIPAM), the block copolymer self-assembled into micelles in an aqueous solution.^[115] The ultrasound-induced SP-to-MC isomerization in the micellization sample was fourfold higher than when dispersed in a dissolved sample (**Figure 17A**). This observation was due to the micelles partially swelling under sonication,

resulting in a larger dielectric constant of the medium around the mechanophores. Microspheres of SP cross-linked within PMA and embedded within polyacrylamide hydrogels,^[106,176] led to substantially improved mechanochromic sensitivity. In addition, using SP as a cross-linker rather than EGDMA in hydrogel formation, led to significantly improved mechanical properties (Figure 17B). It was believed that the covalent bond breakage based on SP-to-MC conversion led to the enhanced toughness. The same polymeric structure was employed to conjugate tri-functional Rh within micelles.^[136] In addition, introduction of side chains, alkyl C18, into the micelles greatly improved the toughness and stretchability of the hydrogels due to crystallization of the long alkyl chains, leading to a higher level of ring-open Rh prior to failure. Enhanced mechanical and mechanochromic properties by integration of mechanophores were also observed in radical-based mechanochromophore systems. DFSN cross-linked PHMA exhibited a significantly higher fracture energy than the PHMA cross-linked with hexamethylene dimethacrylate (HDMA), as the dissociation of DFSN molecules was able to dissipate the energy concentrated at the cross-linked sites.^[154,177]

The transmission and distribution of applied force differ for both linear and cross-linked polymers. For example, linear DABBF-PU dissolved in 1,4-dioxane did not show any color change when frozen in liquid nitrogen, whereas cross-linked DABBF-PU swollen with 1,4-dioxane switched to blue during freezing.^[17] This was reported to be due to the mechanical energy induced by freezing being greater than the bond dissociation energy for DABBF cross-linked in PU (81.0 kJ mol⁻¹), but less than the bond dissociation energy of DABBF in a linear polymer (85.1 kJ mol⁻¹). Interestingly, the cross-linked DABBF-PU in dry and gel states were not responsive to other mechanical loading such as tension and shearing. When DABBF served as a static cross-linker within a PMA matrix, the mechanical properties and dissociation ratio were significantly higher than those of DABBF acting as a movable rotaxane-based cross-linker (structure shown in Scheme 4D).^[151] The color change of D-RCP was insignificant even after fracture. The ratio of DABBF dissociation in cross-linked D-CCP was about four times higher than that in dynamic D-RCP under a specific strain. This was primarily due to DABBF in a sliding cross-linked network being able to dissipate energy and allowing the radicals to rapidly recombine.

Jo et al. showed that when mechanochromophores were incorporated as cross-linkers, their cross-link density could be used to affect the onset of fluorescence in SP-PMMA, with a higher cross-link density resulting in an earlier fluorescence onset.^[178] However, the saturated fluorescence intensity declined with an increase in cross-link density, which was likely caused by a smaller distribution of force on each individual cross-linker. When radical-based mechanochromophores served as the cross-linkers in polymer networks, the cleavage of dynamic C-C linkages weakened the force transmission to activate more mechanochromophores. By introducing extra static cross-linking points, for example into a TASN-PU system, the force transmission was maintained.^[25] Here bisphenol A-tetraol (BPA-tetraol) as a static co-cross-linker functioned as “pillars” to prevent a reorganization of the polymer network when the TASNs dissociated. The efficiency of force transmission by freezing was significantly improved by increasing the ratio of BPA cross-linker.

4.2.2. Orientation of Mechanochromophores, Alignment and Pre-Stretching of Polymer Strands

For bulk polymers, pre-stretching and alignment of polymer strands and the orientation of mechanochromophores significantly facilitate mechanochromic activation. O'Bryan et al. reported a pre-stretched SP-centered PCL film which produced an obvious purple color under deformation along the pre-stretched direction, whereas the color change was minor for the specimen without a pre-stretching step.^[83] In a more recent study, an alternating copolymer P(SP-*alt*-C₁₀) (structure shown in Figure 5B) was processed into nanofibers by electrospinning, with the fibers either aligned or randomly embedded in PDMS.^[96] The fiber-aligned specimen presented a pronounced color change only under stretch along the alignment direction yet showed no distinguishable color-switching under deformation perpendicular to the alignment direction. As a comparison, a randomly aligned-fiber composite displayed a color transition when stretched along both directions, however, the blue color intensity was lower than that of the fiber-aligned specimen (Figure 18). Both studies demonstrated that an alignment of polymer strands can sufficiently enhance the mechano-response on a macroscopic level. A quantitative measurement of MC orientation based on the calculation of anisotropy of fluorescence polarization was performed on an SP-linked PMA elastomer.^[111] The comparison of the order parameter between the UV-activated and stretch-activated specimens under similar strain suggested that the unstrained sample was randomly oriented and the mechanophores preferentially aligned along the deformed direction under strain. This study provided evidence on a molecular level of the importance of mechanophore orientation to mechanochromic response.

An effective approach to in situ pre-stretching mechanochromophore-linked polymer chains was using a multinet network structure. As reported by Ducrot et al., the first-network was pre-stretched by the formation of a second and third-network, and was the key to improved mechanical properties, since the sacrificial bonds in the first-network can absorb the dissipated energy when stretched.^[34] Thus, the strategy of mechanochromophore cross-linked in the first-network has been further adopted to improve mechano-sensitivity. Here, an Rh-containing triple network displayed a high mechano-sensitivity with a threshold strain of around 24%, which was much lower than that of a DN.^[14] The excellent mechanical properties of the triple network also allowed the isomerization to go through different pathways under and after loading for multi-fluorescence color-switching. Zhang and co-workers prepared Rh-containing DN hydrogels via a solvent replacement approach instead of drying before swelling in precursor.^[137] SP was also introduced into a polyacrylate multinet network to improve the mechanochromic sensitivity.^[98] Compared to the elastomer made from mono acrylate, the samples prepared with different types of acrylates in different networks showed an improved mechano-sensitivity and lowered the color activation energy to 0.1 MJ·m⁻³. The multinet network structure also allowed the SP-linked elastomer to achieve a higher mechanochromic activation than photochromic activation. In more studies, an SP-linked PEA multinet network was utilized to analyze stress distribution and crack propagation,^[108] while the SP-linked PEA multinet network exhibited excellent stretchability (3400% strain) when employing

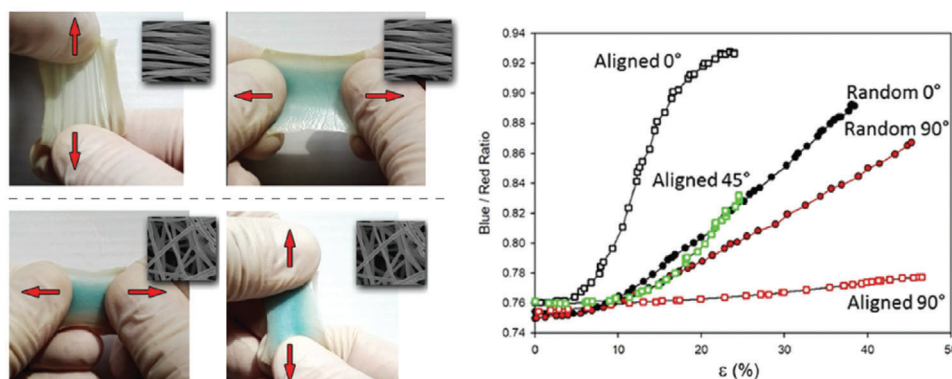


Figure 18. Optical images of P(SP-*alt*-C₁₀)-PDMS composites with aligned fiber and randomly aligned fiber under stretching in vertical or perpendicular directions, and color ratio of blue to red for the two samples elongated in different directions. Reproduced with permission.^[96] Copyright 2018, Wiley-VCH GmbH.

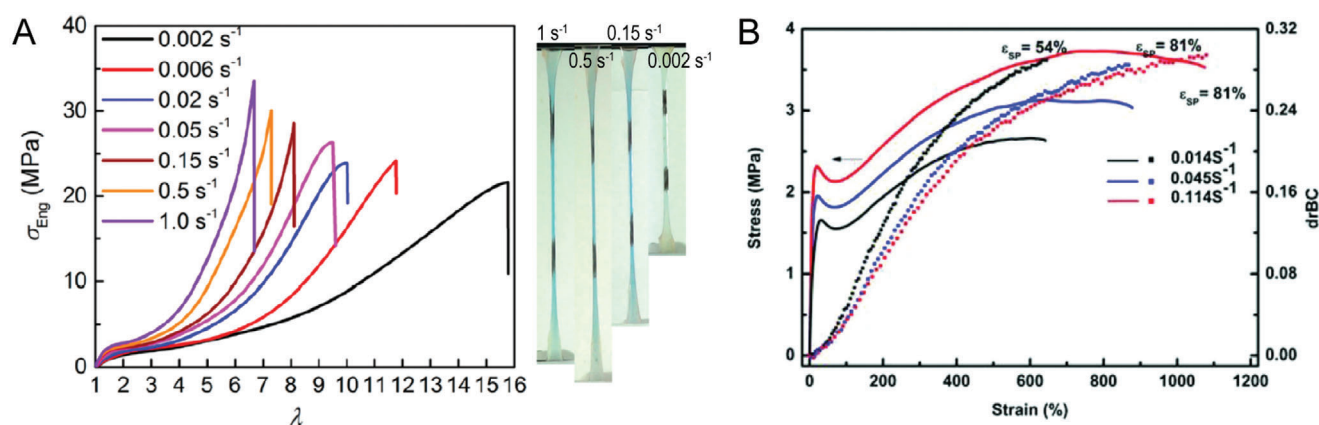


Figure 19. Effect of strain rate on mechanochromic properties. A) Tensile stress–strain curves of dual cross-linked SP-PU elastomers, and optical images of the corresponding specimens stretched to a strain of 600%. Reproduced with permission.^[124] Copyright 2014, American Chemical Society. B) Stress–strain curves of PBA-SP-PS polymers, and the corresponding change of blue color intensity against strain. Reproduced with permission.^[88] Copyright 2018, Wiley-VCH GmbH.

a low cross-linker concentration in the first-network (0.048 mol % to monomer).^[109]

A more direct approach to enhancing the mechano-sensitivity by pre-stretching the polymer network was via swelling the polymers in solvents.^[179] But how to use this solvent swelling strategy in real applications remains unanswered, with regard to the concerns of solvent leakage, volatility, and toxicity.

4.3. Conditions of Mechanical Testing

The methods and conditions of mechanical testing have an effect on the measured mechano-activity of a polymer system.

Strain rate is a well-known element affecting specimens' mechanical properties, but there are two opposite trends for the effect of strain rate on mechano-activation, depending on the polymer matrices. Sotto's group determined that a higher strain rate during testing usually led to a greater mechanochromic response.^[112] It was believed that a higher stress from a higher strain rate facilitated chain alignment, as evidenced by the shifted strain-hardening region. In a dual cross-linked SP-PU system, a

deeper blue color was observed in response to a higher strain rate (Figure 19A), which was consistent with an earlier onset of the strain-hardening region with increasing strain rate.^[124]

In contrast, the opposite trend of the strain rate effect on mechano-response was reported for a glassy SP-linked PMMA under loading at 90 °C. Although a slower strain rate ($1.2 \times 10^{-4} \text{ s}^{-1}$) led to yielding at a relatively low stress, the fluorescence intensity was higher than that of the sample applied with a higher strain rate (1.2×10^{-3} – $1.2 \times 10^{-1} \text{ s}^{-1}$).^[82] The same trend was observed during both tensile and compression tests. This was caused by a longer loading time resulting from a slower strain rate, which allowed more time to promote the SP-to-MC conversion. When the loading time was normalized, the general rule that a faster strain rate results in a higher fluorescence intensity were still applicable. Likewise, a higher tensile strain rate resulting in a slower mechanical activation occurred with glassy-like PBA-SP-PS (Figure 19B).^[88] The same phenomenon was observed for glassy SP-PCL, and a higher strain rate led to color activation within a shorter time.^[130]

The color change for glassy polymers usually occurred after yielding, while the change for elastomers generally emerged

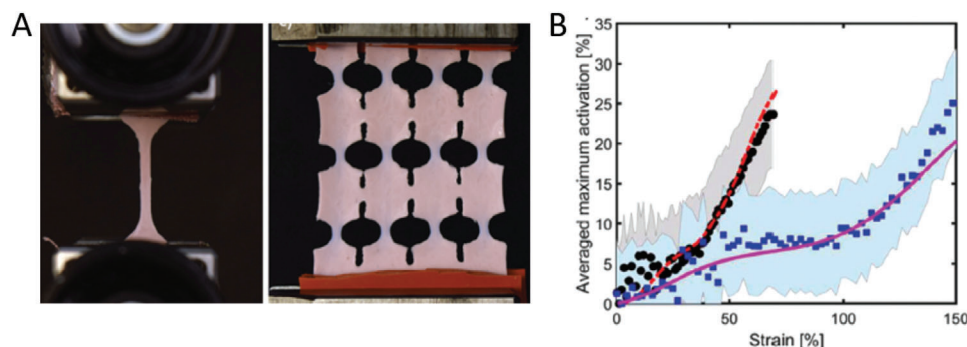


Figure 20. Effect of the specimen shape on mechanochromic response. A) SP-PDMS in dogbone shape (left) and lattice shape (right) at 50% tensile strain. B) Activation ratio of SP for SP-PDMS in the dogbone-shape (blue square) and lattice-shape (black circle) as a function of strain. Reproduced with permission.^[180] Copyright 2020, The Royal Society of Chemistry.

during the strain-hardening region. From this, it would appear that the strain rather than the stress played a more important role in the onset of mechano-activation, whereas the conversion ratio of SP-to-MC more depended on the loading time. In this case, it can explain the opposite trends observed for the effect of strain rate in various polymer systems. Exceptionally, a more recent study suggested that an extremely high strain rate (1000 s^{-1}) of compression led to the onset activation of SP-PDMS elastomer at a lower strain but a higher stress.^[156] It was hypothesized that the critical strain achieved on the bulk matrix dominated the colorimetric onset because the stress was concentrated in a small region of SP containing strands.

Silberstein's group reported the effect of loading modes (tension and compression) on mechanochromic performance.^[82] SP-PMMA specimens subjected to tension or compression under the same conditions (temperature and strain rate) displayed similar mechanical responses, including the onset of activation strain and the performance of higher strain rate leading to higher fluorescence intensity. The only difference was that the compression required a higher stress than tension for color activation. As the majority of the studies in this field used tension to trigger the activation, the mechanism for compression from a molecular level, that is, chain alignment and SP orientation, remains to be further investigated.

The conditions of the samples for mechanical testing, specifically the shape, have shown to have a significant impact on their mechanochromic response.^[180] Schwartz and co-workers compared the mechanochromic activities of SP-PDMS and SP-PCL in dogbone and lattice shapes via tensile testing and computational modeling. As the applied force was localized in the short and thin regions, the color activation occurred at a significantly lower strain in the thin zone (**Figure 20**). This study provides a strategy to lower the mechano-activation threshold using the knowledge of mechanics.

5. Applications

Force-induced color change materials are attractive as they provide optical changes without the need for external monitoring devices.^[181] As the fabrication of mechanochromophore-linked polymers has been well established, the challenge

moves to the implementation of these materials for real-world applications.

5.1. Sensors

The Craig group has been focusing on applying SP-linked PDMS to stress/strain sensing applications,^[90,131,132,164,165,182] where interesting examples such as soft robotic grippers have been reported.^[132] As a proof-of-concept, an SP-PDMS-based balloon started to change color from a 70% biaxial strain induced by inflation. Based on that, the expansion of the robot gripper was not enough to induce an optimized mechanochromic response, but the region with the most intense color provided an indication for a risk of failure (**Figure 21A**). The soft robot could also be used to monitor a spatial environment when a confined space disrupted the inflation. Magrini et al. reported a multilayered bulk composite with damage reporting ability via assembling SP cross-linked poly(2-hydroxyethyl methacrylate)-poly(urethane diacrylate) with glass composite layers.^[183] Fluorescence color changes upon loading were measured in the system.

The development of 3D printing has brought great opportunities to a range of functional materials with complicated structures,^[185–187] and is amenable to processing color-changing materials into customized shapes for sensing functions. The extrusion-based and vat polymerization processes are two of the most common 3D printing technologies, with the former building objects by melting and extruding thermoplastic filament onto a building plate, and the latter by irradiating UV or digital light to photo-polymerizable resins layer by layer. Broadening the options of printable materials is essential for the growth of 3D printing, especially for the development of functional materials that can be used for smart devices.^[188,189] So far, there are only two examples of 3D printed mechanochromophore containing polymers, with both using SP. Mechanochromic SP-PCL was processed into a force sensor by extrusion 3D printing using a fused deposition modeling printer.^[116] Customized specimens with two different SP-PCL were printed via dual extrusion technique. Specifically, a difunctional SP-linked filament responsive to both UV irradiation and mechanical force was embedded as strips in a monofunctional SP-linked filament which

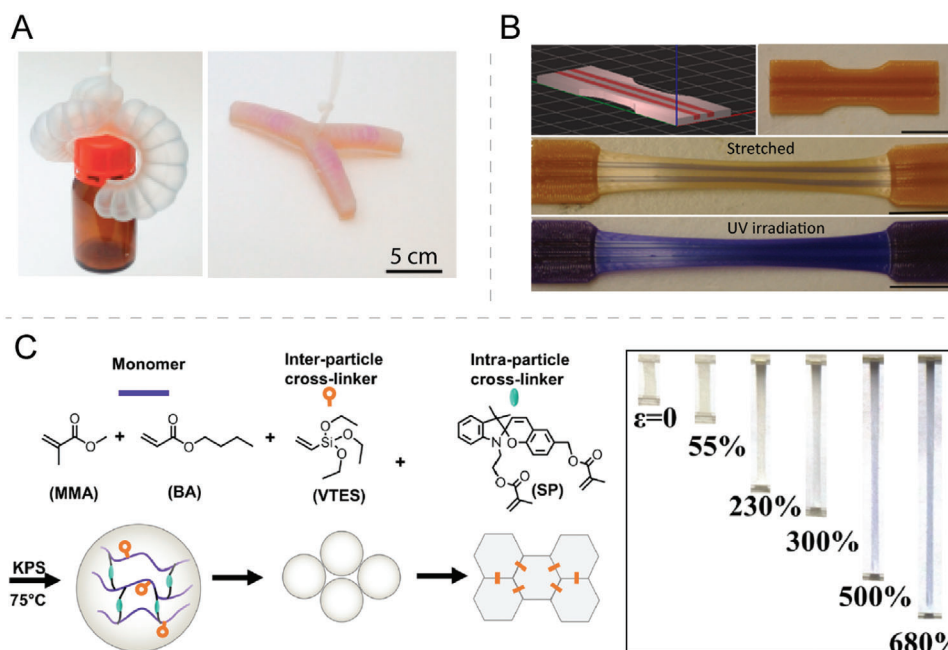


Figure 21. Demonstrated applications of mechanochromic SP-linked polymers as force sensors. A) A three-arm gripper robot. Reproduced with permission.^[132] Copyright 2015, American Chemical Society. B) SP-PCL filament responsive to both UV and mechanical force (red strips) embedded within an SP containing filament only responsive to UV, fabricated via 3D printing. Scale bar = 20 mm. Reproduced with permission.^[116] Copyright 2015, American Chemical Society. C) SP-containing latex film showing different colors at various strains. Reproduced with permission.^[184] Copyright 2017, American Chemical Society.

was only UV-responsive (Figure 21B). Therefore, only the strips displayed color switching under deformation, whereas the whole sample turned purple under UV irradiation. Recently, the Craig group reported a mechanochromic silicone ink for extrusion 3D printing^[190] which employed printable inks reported by Sangchul et al.^[191] SP was first incorporated into uncured PDMS then mixed with stiffer PDMS microbeads. A sol-gel transition occurred during the mixing process due to formation of capillary bridges. The resultant uncured silicone ink with suitable yielding stress and shear-thinning properties could be extruded and printed. In the printed sample, SP located at the “bridges” between the microbeads, where the stress was concentrated under deformation, facilitated the mechano-activation. However, this printing technique required an hours-long post thermo-curing step. An advantage of this printable PDMS ink over the PCL filament is that the PDMS specimen was shape recoverable.

Acrylic latexes are widely used in daily life, such as in paints and adhesives. Water-based acrylic latexes are under rapid development to replace the solvent-based latexes in order to reduce the toxicity to human health and the environment. Emulsion polymerization is a current approach to solidifying coated films.^[192,193] Li et al. incorporated difunctional SP with methyl acrylate groups into acrylic latexes via emulsion polymerization to prepare mechanochromic latex films that could sense deformation (Figure 21C).^[184] Siloxane monomer vinyltriethoxysilane (VTEA) was used to form cross-links between the latex particles via hydrolysis and condensation during the film formation, which improved mechanical properties for the latex films. The latex films displayed significant color change over 300% strain and could be stretched up to 680% strain. It was the first example of a

mechanochromic acrylic latex and offered a potential application in force-responsive and self-reporting coatings.

5.2. Electronic Devices

Devices containing deformable components combined with mechanochromic polymers for visualization or optical monitoring purposes have been investigated.^[131] Deformation can be caused directly by external stress or indirectly from other stimuli, such as electrical signals. Mechanochromic SP-PDMS was employed to assemble an electro-mechano-chemically responsive system, reported by Wang et al.^[131] It was a laminated device consisting of a buffer elastomer underneath an SP-PDMS elastomer, a protective insulator, a metal foil at the bottom, and a compliant electrode on the top surface. The flat surface of SP-PDMS wrinkled when an electric field was applied, resulting in craters forming. Strain over 600% occurred to the crater edges at a high electric field above 45 kV mm⁻¹. At this point, a significant fluorescence could be observed due to the SP-MC conversion. Different deformed patterns were designed by pre-stretching the mechanochromic elastomers or embedding rigid objects.

Metallic nanowires such as silver nanowire (AgNW) are suitable for fabricating displays, wearable electronics, and touch sensors due to their excellent flexibility, conductivity, and optical transparency.^[194,195] In an extension of this, Cho et al. investigated an SP-PDMS elastomer assembled with AgNW electrodes toward force-responsive touch screens (Figure 22A).^[164] The SP-PDMS film was coated on the top of a cross-aligned AgNW electrode layer, which was connected to a

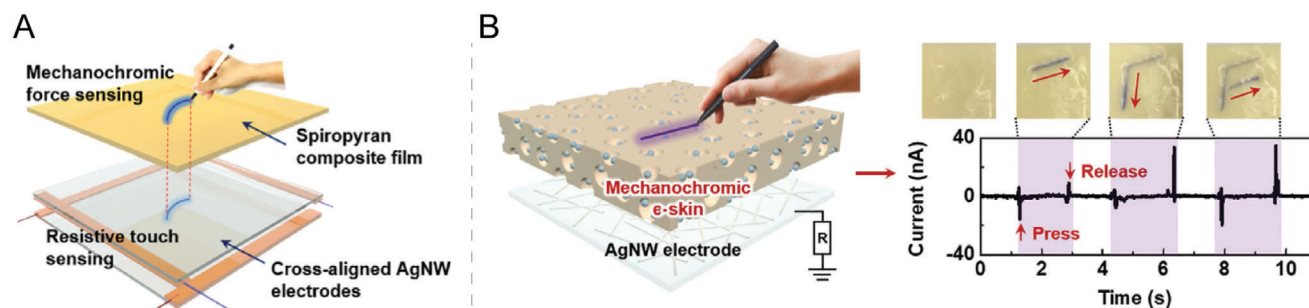


Figure 22. Applications of SP-linked mechanochromic polymers in electronic devices. A) Schematic structure of a pressure-sensitive touch screen with color change in response to dynamic writing. Reproduced with permission.^[164] Copyright 2017, American Chemical Society. B) Schematic diagram of a dual-mode force sensor with mechanochromic and triboelectric functions using a porous nanoparticle-in-micropore SP-PDMS. Reproduced with permission.^[165] Copyright 2019, Wiley-VCH GmbH.

laptop computer via a four-wire resistive controller board and equipped with a spectroradiometer. The touch screen was highly transparent and flexible, with the capabilities of quantifying the writing force level and tracing the location of writing via analyzing the generated color. In another work, hierarchical nanoparticles-in-micropore architecture was adopted to prepare porous mechanochromic SP-PDMS composites to enhance the mechanochromic sensitivity.^[165] The composites could be stretched up to a strain of 400% and the color change was reversible with a stable mechanochromic performance under a strain of 250% for 100 cycles. The porous composite was combined with AgNW to set up a dual-functional, mechanochromic, and triboelectric force sensor which was able to detect writing force and speed and acoustic signals (Figure 22B). The key in the design of multi-functional devices employing these mechanochromic materials is to improve the mechanochromic sensitivity, specifically lower the activation strain and force.

Mechanochromic stretchable electronics are another category of applications where a combination of mechanochromic polymers with metallic materials has been reported for the purpose of failure sensing.^[90] Here, eutectic gallium indium alloy was embedded into SP-PDMS elastomers via injection of the conductive liquid metal into the PDMS films consisting of microchannels. Stretching the liquid metal device to a large strain was accompanied by a mechanochromic response. Since the wire failed at 125–160% strain and the color change of SP-PDMS began at 90% strain, the remarkable color gave an indication that the wire was under a risk of failure if it was further stretched.

SP has also been incorporated into ionic conductive gels to fabricate mechanochromic ionotronics.^[196] Here, a micellar structure was employed to conjugate SP to protect the ring-closed SP from isomerizing into MC prior to an external stimuli. The gel sensors performed analogous functions to human skin, including sensing mechanical stimuli (touch) and color change (bruising) when subjected to heavy loads.

5.3. Multi-Color Switching

Since the coloration of mechanochromophore-based materials is caused by a change in chemical structure, the majority of materials only display two different colors. Materials with multi-color transitions are desirable to improve the scope of sensor appli-

cations or enrich the visualization function stimulated by force for electronic devices. A multi-color switching system containing two different mechanochromophores in polymer/silica composite has been developed by the Otsuka group.^[141] Here, a combination of blue from dissociated DABBF radicals and orange from ring-open NPs was employed, in order to achieve a third green color upon activation. DABBFs were mainly connected at the interfaces and NPs were conjugated in the polymer domains. Upon grinding, the composite changed color from yellow to blue then green because the DABBF molecules at the interface were activated before the ring-opening of NPs in the polymer domains (Figure 23A). Molecular simulations demonstrated that the barrier of bond cleavage for DABBF dissociation was lower than that for NP ring-opening when under a relatively low external force, and the barriers for both mechanochromophores became similar when the force was increased (Figure 23B). In addition, the recombination of DABBF was accelerated by addition of organic solvent due to the increased molecular mobility, which barely affected the ring-closure of MC, resulting in the color transition from green to orange then yellow; the ring-closure of MC could be sped up by visible light irradiation, which had little impact on the recombination of the radicals.

Chen and co-workers synthesized a segmented PU containing mechanochromic Rh and mechanoluminescent 1,2-dioxane in the hard domains.^[197] A lower strain was required for the activation of Rh than that for 1,2-dioxane, enabling visualization of applied force at a broader range. Therefore, red coloration was first observed, followed by red chemiluminescence with increasing stress.

Another material with a multi-color transition was developed by Otsuka's group, combining the mechanochromophores of DABBF, DABBT, and TASN (Figure 24A).^[21] Incorporating these mechanochromophores into the same matrix at different locations was also reported by the same group for multi-color switching.^[22] Specifically, TASN was embedded at the center of PS chains which served as hard domains, while DABBT as a core was connected to four PS-*b*-PMA chains to construct star-shaped polymers where the PMA served as soft domains (Figure 24B). The blended mixture of TASN-PS and DABBT-(PS-*b*-PMA) changed color from colorless to green under stretching, yet yellow/green upon grinding. The mechanism for this change was that DABBTs in soft PMA were easier to deform than the TASNs in hard PS during stretching, whereas the force of

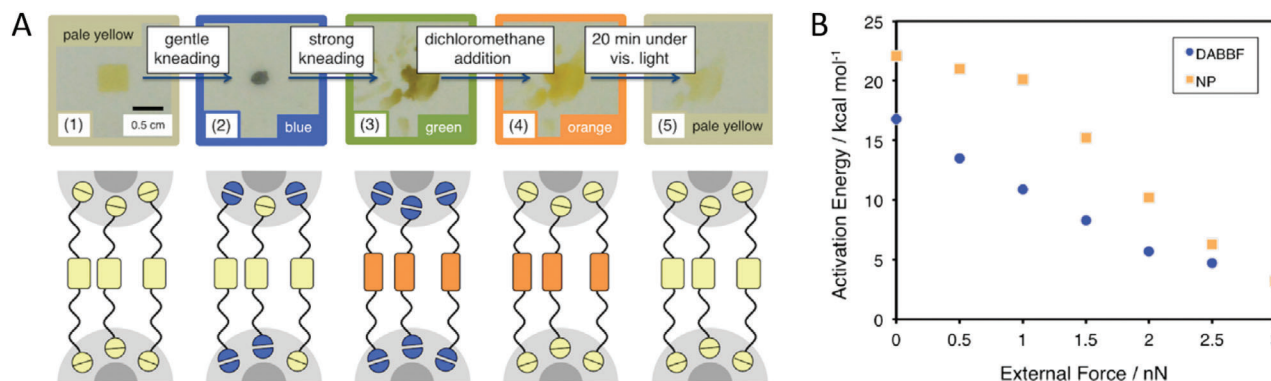


Figure 23. Multi-color switching of a DABBF-NP-linked polymer/silica composite upon kneading. A) Images and graphic illustrations of the bulk sample under kneading, adding DCM and visible light irradiation. B) Energy barriers for DABBF dissociation and NP ring-opening based on molecular simulations. Reproduced with permission.^[141] Copyright 2019, American Chemical Society.

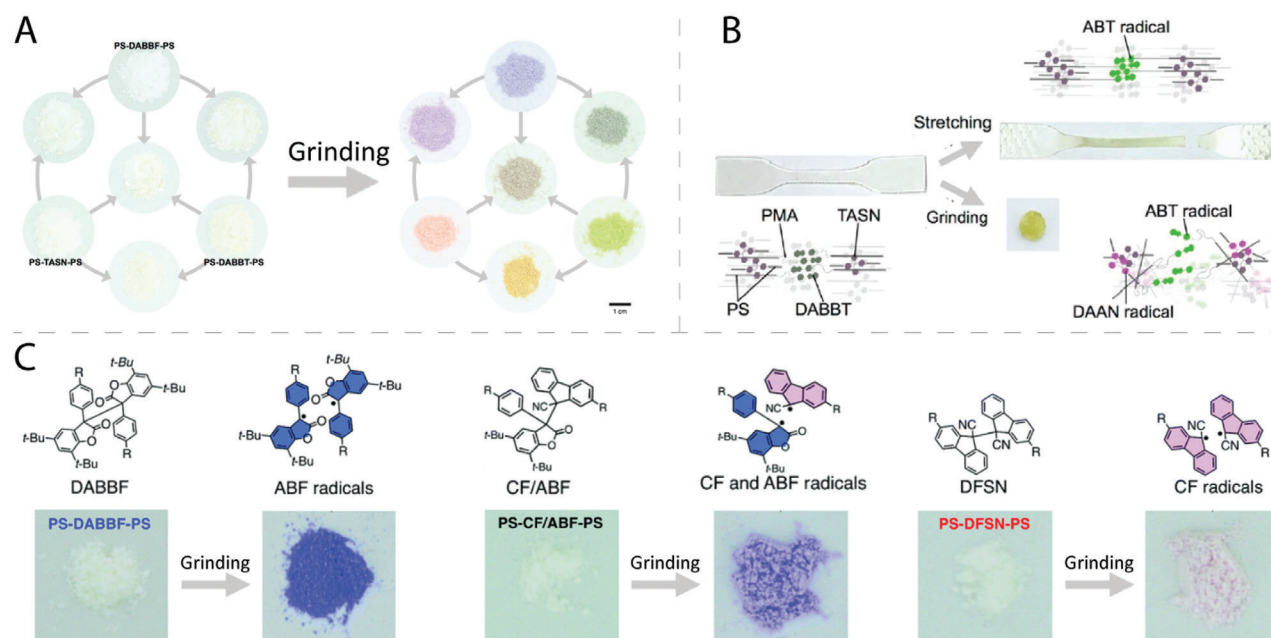


Figure 24. Multi-color switching systems via combining different radical-based mechanochromophores. A) Mixtures of DABBF-PS, DABBT-PS and TASN-PS before and after grinding. Reproduced with permission.^[121] Copyright 2018, Wiley-VCH GmbH. B) Images and proposed mechanism of TASN-PS and DABBT-(PS-b-PMA) blended sample before and after stretching and grinding. Reproduced with permission.^[122] Copyright 2017, American Chemical Society. C) Structures and photos of a non-symmetric radical-based mechanochromophore derived from DABBF and DFSN before and after grinding. Reproduced with permission.^[198] Copyright 2021, The Royal Society of Chemistry.

grinding was able to dissociate both DABTTs in PMA and TASNs in PS. More recently, the difference in mechano-sensitivity between mechanophore-linked star and linear polymers was utilized to show multi-color switching under different loading conditions.^[199] DABBF-centered PS star with a higher molecular weight and DABBT-centered linear PS with a lower molecular weight were blended. Upon grinding, the color changed from white to blue due to the higher mechano-sensitivity of DABBF-centered PS star, then to gray because of the activation of both DABBF and DABBT upon a longer time of grinding. A non-symmetric mechanochromophore based on radical-exchange between DABBF and DFSN was also reported for tuning the mechano-response, which showed a combined color of blue

and pink from dissociated DABBF and DFSN respectively upon grinding (Figure 24C).^[198]

White fluorescence, under deformation, has been achieved by incorporating pyrene groups into a Rh-linked P_nBA triple-network.^[135] Prior to stretching, the combination of green fluorescence from the pyrene excimer, blue fluorescence from monodispersed pyrene, and ring-closed Rh provided the elastomer with blue-green fluorescence. Upon deformation, the ring-open Rh isomer exhibited red fluorescence, leading to a white fluorescence as a result of the combination of blue, green, and red. In addition, the visible color only switched between colorless and pink as the pyrenes generated fluorescence color but not visible color. In another work, multi-color-changing

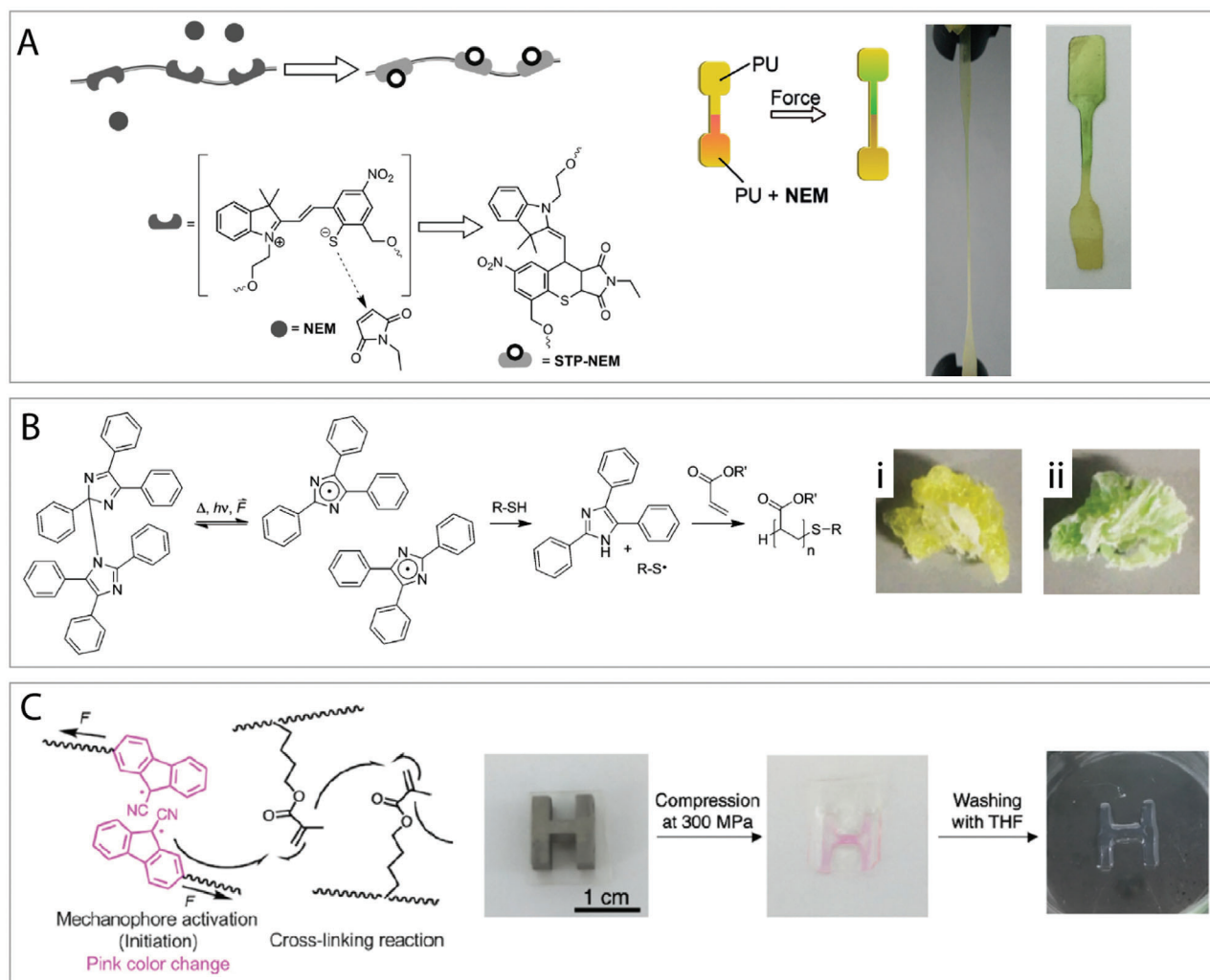


Figure 25. Mechanochemical coloration and polymerization from mechanochromophore-linked polymers. A) Thiol-ene click addition between force-induced TMC and NEM. Reproduced with permission.^[12] Copyright 2016, Wiley-VCH GmbH. B) Paths for HABI dissociation, hydrogen abstraction by TPI and polymerization initiated by the resulted thiyl radicals, and images of HABI-PU i) before and ii) after freezing in liquid nitrogen. Reproduced with permission.^[78] Copyright 2016, The Royal Society of Chemistry. C) Radical polymerization of pendant methacryloyl groups within DFSN-linked PU upon loading, and images of the film after compression and washed with solvent. Reproduced with permission.^[201] Copyright 2021, Wiley-VCH GmbH.

was realized by introducing various mechanochromophores into different networks of a multinet system, where an anthracene-maleimide adduct was introduced into the first-network while Rh was cross-linked in the second-network.^[200] Upon stretching, the material showed blue fluorescence and further to red-violet with increasing tensile stress. This was reported to be the result of the anthracene derivative forming initially from anthracene-maleimide adduct dissociation prior to Rh activation in the ring-open form, with blue fluorescence and red fluorescence generated for the former and latter, respectively.

5.4. Force-Induced Coloration and Chemical Reactions

Inspired by the properties of photoactivating thiol Michael addition of TMC,^[202] synthetic STP-linked PES and PU were used to show dual mechanical responses, including mechanochromism

and a loading-induced addition reaction.^[12] When the polymers were subjected to external force, the generated TMC with a thiol group would react with the double bond on *N*-ethylmaleimide (NEM), resulting in a loading-induced thiol-ene click reaction and an irreversible color switch (yellow color) (**Figure 25A**). When half of the STP-PU sample was doped with NEM, the doped half stayed yellow whereas the half without NEM turned to green upon stretching, demonstrating a reaction between TMC and NEM. In addition, a mechanochemical reaction cascade was designed for a better control of loading-induced strengthening of mechanochromic polymers.^[142] The cascade, based on comb polymers containing STP and anthracene/maleimide adduct in the side chain, involved three reactions, including ring-opening of STP into TMC, Michael addition of TMC to maleimide, and dissociation of anthracene/maleimide adducts. A moderate loading force can trigger the dissociation of anthracene/maleimide adducts releasing maleimide species, while a smaller force can

induce ring-opening of STP to TMC. Therefore, the two reactions provided reagents for an addition reaction, leading to polymer cross-linking. Thus, the loading strengthening can be modulated by the kinetics of the dissociation of anthracene/maleimide adducts rather than only by the conversion of STP-to-TMC.

Verstraeten et al. utilized TPI radicals generated from HABI dissociation to abstract hydrogens from thiol groups to form thiyl radicals, which were capable of initiating radical polymerizations (Figure 25B).^[78] When the HABI-PU, swollen with MA and methyl 3-mercaptopropionate, was frozen in liquid nitrogen, the sample color changed and the NMR spectra showed a disappearance of peaks for MA and an appearance of peaks for PMA, suggesting a radical polymerization initiated by HABI dissociation. In another study, making use of the reactivity of TASN-derived radicals towards vinyl monomers, a cross-linked TASN-PU gel swollen in a mixed solution of solvent and fluorescent monomer was designed.^[203] It showed freezing-induced activation to pink radicals, which initiated an insertion of monomer into the C–C bond of TASN, to achieve post-modification of the polymer network.

The radicals generated from dissociated DFSN under mechanical stimuli have also been shown to be capable of initiating radical polymerization.^[201] The Otsuka group designed a segmented PU with DFSN located in the soft segment and methacryloyl groups in the side chains (Figure 25C). When external force was applied, the DFSN in the PU sample dissociated into pink radicals. These radicals can trigger polymerization of the methacrylate in the stressed area to realize a strengthening function via mechanical stimuli. The difference between this design from the aforementioned examples in this section was that the monomer was attached to the polymer matrix, rather than from an external source. These studies demonstrated the ability to use the mechanism of destructive chemistry to achieve constructive outcomes.

6. Conclusion and Future Perspectives

Colorimetric materials responsive to mechanical force have drawn much attention due to their translation of force into fascinating optical changes. As a subclass mechanochromophore-linked polymeric materials have gained significant progress in the past decade. This review has summarized isomerization-based and radical-based mechanochromophores with visible color changes, and their integration into polymeric materials, including the synthesis, polymer architectures, factors impacting mechanochromic behaviors, and potential applications, with particular focus on SP which has been the most widely studied.

Despite these advances in mechanochromic materials, versatile and standardized characterization methods are needed to directly compare such materials to improve and transfer them to practical applications. Most research groups employ their own characterization methods, which brings difficulties in comparing these different materials. For example, a comparison of the different optical properties between radical- and isomerization-based mechanochromophores has not been shown, as EPR spectrum is the main method used to characterize the former but is not applicable to the latter. For bulk materials, sample dimensions/shape and testing conditions have a significant effect on their mechanochemical properties. The non-consistent testing parameters among different systems are a big challenge when

choosing a specific mechanochromic product for a targeted application.

Ionic or polar environments are not ideal for the reversible conversion between SP and MC, thus restricting the available options for polymer matrices. The use of coordination between charged MC and metals enables reversible cross-links triggered by force. However, in this situation, suppressing the spontaneous isomerization of SP to MC under an ionic environment is vital for utilizing the metal-MC coordination.^[134] Notably, the issue has rarely been reported with other mechanochromophores, which provides some possibilities to design more controllable mechanochromic systems in polar environments. Radical-based mechanochromophores have been less investigated than the isomerization-based mechanochromophores, however, their unique properties, especially the radical generation under mechanical stimuli, deserves deeper investigations for a wider use.

One of the challenges lacking in the current approaches is the ability to regulate the mechano-sensitivity, specifically, tailorable onset strain/stress of color activation and controllable activation levels. Multinetwork structures can significantly reduce the energy of color activation, however, the range of activation energy is narrow. For targeted applications, such as indicators for fracture prevention, a deep color change prior to fracture strain is essential, but it is still difficult to match these transition points for many versatile polymers. An alternative approach to manipulating the mechano-sensitivity is to develop multi-color switching systems, where the color transition corresponds to different levels of strain or force, enabling a more direct visualization of force than a single color-switching material. As the color-changing of mechanophore-linked materials is based on the chemical structure of the molecules, multi-color switching requires more thoughtful design, especially for materials in the bulk state. A rational design is to incorporate multiple mechanochromophores into a single matrix to achieve an array of colors, yet this remains to be further explored. Another desirable strategy would be to combine the mechanochromophore-linked materials with the materials that have structural colors, since structural colors based on light reflection can cover a wide range of wavelengths when subjected to external force.^[204] We believe a promising direction for these materials is to develop easily tunable mechanochromic systems capable of multi-color change.

Currently, the potential applications of the well-established mechanochromic polymer materials mainly focus on visualization of stress distribution and warning of mechanical failure. The issues remaining to be answered include the chemical stability of mechanochromophores after long-term use, costly synthetic routes, and facile scale-up fabrication. One proof-of-concept application is transferring the disruptive chemistry (bond cleavage) to constructive chemistry (new bond formation), which expands the field beyond the main concept presented here of mechanical force leading to destruction.^[4]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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- [1] M. K. Beyer, H. Clausen-Schaumann, *Chem. Rev.* **2005**, *105*, 2921.
- [2] M. A. Ghanem, A. Basu, R. Behrou, N. Boechler, A. J. Boydston, S. L. Craig, Y. Lin, B. E. Lynde, A. Nelson, H. Shen, D. W. Storti, *Nat. Rev. Mater.* **2020**, *6*, 84.
- [3] G. Kaupp, *CrystEngComm* **2009**, *11*, 388.
- [4] J. Li, C. Nagamani, J. S. Moore, *Acc. Chem. Res.* **2015**, *48*, 2181.
- [5] Y. Chen, G. Mellot, D. van Luijk, C. Creton, R. P. Sijbesma, *Chem. Soc. Rev.* **2021**, *50*, 4100.
- [6] J. Wang, I. Piskun, S. L. Craig, *ACS Macro Lett.* **2015**, *4*, 834.
- [7] J. N. Brantley, K. M. Wiggins, C. W. Bielawski, *Polym. Int.* **2013**, *62*, 2.
- [8] C. Calvino, L. Neumann, C. Weder, S. Schrettl, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 640.
- [9] M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755.
- [10] R. W. Barber, M. E. McFadden, X. Hu, M. J. Robb, *Synlett* **2019**, *30*, A.
- [11] R. Klajn, *Chem. Soc. Rev.* **2014**, *43*, 148.
- [12] H. Zhang, F. Gao, X. Cao, Y. Li, Y. Xu, W. Weng, R. Boulatov, *Angew. Chem., Int. Ed.* **2016**, *55*, 3040.
- [13] Z. Wang, Z. Ma, Y. Wang, Z. Xu, Y. Luo, Y. Wei, X. Jia, *Adv. Mater.* **2015**, *27*, 6469.
- [14] T. Wang, N. Zhang, J. Dai, Z. Li, W. Bai, R. Bai, *ACS Appl. Mater. Interfaces* **2017**, *9*, 11874.
- [15] K. Guo, Y. Chen, *Mater. Chem. Phys.* **2013**, *137*, 1062.
- [16] M. J. Robb, T. A. Kim, A. J. Halmes, S. R. White, N. R. Sottos, J. S. Moore, *J. Am. Chem. Soc.* **2016**, *138*, 12328.
- [17] K. Imato, A. Irie, T. Kosuge, T. Ohishi, M. Nishihara, A. Takahara, H. Otsuka, *Angew. Chem., Int. Ed.* **2015**, *54*, 6168.
- [18] K. Imato, T. Kanehara, T. Ohishi, M. Nishihara, H. Yajima, M. Ito, A. Takahara, H. Otsuka, *ACS Macro Lett.* **2015**, *4*, 1307.
- [19] T. Kosuge, K. Imato, R. Goseki, H. Otsuka, *Macromolecules* **2016**, *49*, 5903.
- [20] K. Imato, H. Otsuka, *Polymer* **2018**, *137*, 395.
- [21] K. Ishizuki, H. Oka, D. Aoki, R. Goseki, H. Otsuka, *Chem. - Eur. J.* **2018**, *24*, 3170.
- [22] K. Ishizuki, D. Aoki, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2018**, *7*, 556.
- [23] T. Sumi, R. Goseki, H. Otsuka, *Chem. Commun.* **2017**, *53*, 11885.
- [24] S. Kato, K. Ishizuki, D. Aoki, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2018**, *7*, 1087.
- [25] S. Kato, D. Aoki, H. Otsuka, *Polym. Chem.* **2019**, *10*, 2636.
- [26] H. Sakai, T. Sumi, D. Aoki, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2018**, *7*, 1359.
- [27] K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara, H. Otsuka, *Angew. Chem., Int. Ed.* **2012**, *51*, 1138.
- [28] K. Imato, J. C. Natterodt, J. Sapkota, R. Goseki, C. Weder, A. Takahara, H. Otsuka, *Polym. Chem.* **2017**, *8*, 2115.
- [29] J. Li, T. Shiraki, B. Hu, R. A. Wright, B. Zhao, J. S. Moore, *J. Am. Chem. Soc.* **2014**, *136*, 15925.
- [30] D. C. Church, G. I. Peterson, A. J. Boydston, *ACS Macro Lett.* **2014**, *3*, 648.
- [31] H. Zhang, D. Zeng, Y. Pan, Y. Chen, Y. Ruan, Y. Xu, R. Boulatov, C. Creton, W. Weng, *Chem. Sci.* **2019**, *10*, 8367.
- [32] P. Froimowicz, H. Frey, K. J. M. r. c. Landfester, *Macromol. Rapid Commun.* **2011**, *32*, 468.
- [33] Y. Chen, A. J. Spiering, S. Karthikeyan, G. W. Peters, E. W. Meijer, R. P. Sijbesma, *Nat. Chem.* **2012**, *4*, 559.
- [34] E. Ducrot, Y. Chen, M. Bulters, R. P. Sijbesma, C. Creton, *Science* **2014**, *344*, 186.
- [35] J. H. Day, *Chem. Rev.* **1963**, *63*, 65.
- [36] E. Fischer, Y. Hirshberg, *J. Chem. Soc.* **1952**, *868*, 4522.
- [37] M. Nogami, Y. Abe, *J. Mater. Sci.* **1995**, *30*, 5789.
- [38] G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741.
- [39] G. Such, R. A. Evans, L. H. Yee, T. P. Davis, *J. Macromol. Sci., Polym. Rev.* **2003**, *43*, 547.
- [40] L. Florea, D. Diamond, F. Benito-Lopez, *Macromol. Mater. Eng.* **2012**, *297*, 1148.
- [41] L. Kortekaas, W. R. Browne, *Chem. Soc. Rev.* **2019**, *48*, 3406.
- [42] S. L. Potisek, D. A. Davis, N. R. Sottos, S. R. White, J. S. Moore, *J. Am. Chem. Soc.* **2007**, *129*, 13808.
- [43] D. A. Davis, A. Hamilton, J. Yang, L. D. Cremer, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore, N. R. Sottos, *Nature* **2009**, *459*, 68.
- [44] B. Zuo, M. Wang, B.-P. Lin, H. Yang, *Chem. Mater.* **2018**, *30*, 8079.
- [45] Q. Dou, S. S. Liow, W. Weng, X. J. Loh, *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 2837.
- [46] Y. Shiraishi, R. Miyamoto, T. Hirai, *Org. Lett.* **2009**, *11*, 1571.
- [47] H. I. Lee, W. Wu, J. K. Oh, L. Mueller, G. Sherwood, L. Peteanu, T. Kowalewski, K. Matyjaszewski, *Angew. Chem., Int. Ed.* **2007**, *46*, 2453.
- [48] C. Liu, D. Yang, Q. Jin, L. Zhang, M. Liu, *Adv. Mater.* **2016**, *28*, 1644.
- [49] K. Feng, N. Xie, B. Chen, L.-P. Zhang, C.-H. Tung, L.-Z. Wu, *Macromolecules* **2012**, *45*, 5596.
- [50] S. Son, E. Shin, B. S. Kim, *Biomacromolecules* **2014**, *15*, 628.
- [51] D. He, Y. Arisaka, K. Masuda, M. Yamamoto, N. Takeda, *Acta Biomater.* **2017**, *51*, 101.
- [52] Z. Cao, Q. Bian, Y. Chen, F. Liang, G. Wang, *ACS Macro Lett.* **2017**, *6*, 1124.
- [53] J. ter Schiphorst, S. Coleman, J. E. Stumpel, A. Ben Azouz, D. Diamond, A. P. H. J. Schenning, *Chem. Mater.* **2015**, *27*, 5925.
- [54] C. Delaney, P. McCluskey, S. Coleman, J. Whyte, N. Kent, D. Diamond, *Lab Chip* **2017**, *17*, 2013.
- [55] J. T. Wojtyk, P. M. Kazmaier, E. Buncel, *Chem. Mater.* **2001**, *13*, 2547.
- [56] P. J. Wu, J. L. Chen, C. P. Chen, Y. H. Chan, *Chem. Commun.* **2013**, *49*, 898.
- [57] T. Niazov, B. Shlyahovsky, I. Willner, *J. Am. Chem. Soc.* **2007**, *129*, 6374.
- [58] C. Bronner, G. Schulze, K. J. Franke, J. I. Pascual, P. Tegeder, *J. Phys.: Condens. Matter* **2011**, *23*, 484005.
- [59] J. Sunamoto, K. Iwamoto, M. Akutagawa, M. Nagase, H. Kondo, *J. Am. Chem. Soc.* **1982**, *104*, 4904.
- [60] F. Ciardelli, D. Fabbri, O. Pieroni, A. Fissi, *J. Am. Chem. Soc.* **1989**, *111*, 3470.
- [61] J. Zhou, Y. Li, Y. Tang, F. Zhao, X. Song, E. Li, *J. Photochem. Photobiol., A* **1995**, *90*, 117.
- [62] W. Tian, J. Tian, *Dyes Pigm.* **2014**, *105*, 66.
- [63] K. Kinashi, S. Nakamura, M. Imamura, K. Ishida, Y. Ueda, *J. Phys. Org. Chem.* **2012**, *25*, 462.
- [64] Z. Guo, W. Zhu, Y. Xiong, H. Tian, *Macromolecules* **2009**, *42*, 1448.
- [65] Q. M. Zhang, W. Wang, Y.-Q. Su, E. J. M. Hensen, M. J. Serpe, *Chem. Mater.* **2015**, *28*, 259.
- [66] J. ter Schiphorst, M. van den Broek, T. de Koning, J. N. Murphy, A. P. H. J. Schenning, A. C. C. Esteves, *J. Mater. Chem. A* **2016**, *4*, 8676.

- [67] H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim, J. Yoon, *Chem. Soc. Rev.* **2008**, 37, 1465.
- [68] M. Beija, C. A. Afonso, J. M. Martinho, *Chem. Soc. Rev.* **2009**, 38, 2410.
- [69] M. Tian, X. Peng, J. Fan, J. Wang, S. Sun, *Dyes Pigm.* **2012**, 95, 112.
- [70] L. Liu, P. Guo, L. Chai, Q. Shi, B. Xu, J. Yuan, X. Wang, X. Shi, W. Zhang, *Sens. Actuators, B* **2014**, 194, 498.
- [71] V. Dujols, F. Ford, A. W. Czarnik, *J. Am. Chem. Soc.* **1997**, 119, 7386.
- [72] J. Y. Kwon, Y. J. Jang, Y. J. Lee, K. M. Kim, M. S. Seo, W. Nam, J. Yoon, *J. Am. Chem. Soc.* **2005**, 127, 10107.
- [73] V. I. Minkin, *Chem. Rev.* **2004**, 104, 2751.
- [74] Y. Shiraishi, K. Tanaka, E. Shirakawa, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, *Angew. Chem., Int. Ed.* **2013**, 52, 8304.
- [75] J. Plaček, F. Szócs, D. Braun, T. Skrzek, *Macromol. Chem. Phys.* **1994**, 195, 463.
- [76] K. Kawasaki, D. Aoki, H. Otsuka, *Macromol. Rapid Commun.* **2020**, 41, 1900460.
- [77] D. Ahn, S. S. Sathe, B. H. Clarkson, T. F. Scott, *Dent. Mater.* **2015**, 31, 1075.
- [78] F. Verstraeten, R. Gostl, R. P. Sijbesma, *Chem. Commun.* **2016**, 52, 8608.
- [79] D. Ahn, S. R. Zavada, T. F. Scott, *Chem. Mater.* **2017**, 29, 7023.
- [80] S.-L. Xiang, Q.-X. Hua, W.-L. Gong, N.-H. Xie, P.-J. Zhao, G. J. Cheng, C. Li, M.-Q. Zhu, *ACS Appl. Mater. Interfaces* **2019**, 11, 23623.
- [81] J. R. Hemmer, P. D. Smith, M. van Horn, S. Alnemrat, B. P. Mason, J. R. de Alaniz, S. Osswald, J. P. Hooper, *J. Polym. Sci., Part B: Polym. Phys.* **2014**, 52, 1347.
- [82] J. W. Kim, Y. Jung, G. W. Coates, M. N. Silberstein, *Macromolecules* **2015**, 48, 1335.
- [83] G. O'Bryan, B. M. Wong, J. R. McElhanon, *ACS Appl. Mater. Interfaces* **2010**, 2, 1594.
- [84] G. R. Gossweiler, G. B. Hewage, G. Soriano, Q. Wang, G. W. Welshofer, X. Zhao, S. L. Craig, *ACS Macro Lett.* **2014**, 3, 216.
- [85] S. Jiang, L. Zhang, T. Xie, Y. Lin, H. Zhang, Y. Xu, W. Weng, L. Dai, *ACS Macro Lett.* **2013**, 2, 705.
- [86] W. Qiu, P. A. Gurr, G. da Silva, G. G. Qiao, *Polym. Chem.* **2019**, 10, 1650.
- [87] M. Li, Q. Zhang, S. Zhu, *Polymer* **2016**, 99, 521.
- [88] Y. Jia, W.-J. Wang, B.-G. Li, S. Zhu, *Macromol. Mater. Eng.* **2018**, 303, 1800154.
- [89] M. H. Barbee, T. Kouznetsova, S. L. Barrett, G. R. Gossweiler, Y. Lin, S. K. Rastogi, W. J. Brittain, S. L. Craig, *J. Am. Chem. Soc.* **2018**, 140, 12746.
- [90] M. H. Barbee, K. Mondal, J. Z. Deng, V. Bharambe, T. V. Neumann, J. J. Adams, N. Boechler, M. D. Dickey, S. L. Craig, *ACS Appl. Mater. Interfaces* **2018**, 10, 29918.
- [91] M. Sommer, H. Komber, *Macromol. Rapid Commun.* **2013**, 34, 57.
- [92] M.-K. Ng, J. Yang, *Synthesis* **2006**, 2006, 3075.
- [93] H. Komber, S. Müllers, F. Lombeck, A. Held, M. Walter, M. Sommer, *Polym. Chem.* **2014**, 5, 443.
- [94] L. Metzler, T. Reichenbach, O. Brügger, H. Komber, F. Lombeck, S. Müllers, R. Hanselmann, H. Hillebrecht, M. Walter, M. Sommer, *Polym. Chem.* **2015**, 6, 3694.
- [95] F. Kempe, O. Brügger, H. Buchheit, S. N. Momm, F. Riehle, S. Hameury, M. Walter, M. Sommer, *Angew. Chem., Int. Ed.* **2018**, 57, 997.
- [96] M. Raisch, D. Genovese, N. Zaccheroni, S. B. Schmidt, M. L. Focarete, M. Sommer, C. Gualandi, *Adv. Mater.* **2018**, 30, 1802813.
- [97] W. Qiu, P. A. Gurr, G. G. Qiao, *ACS Appl. Mater. Interfaces* **2019**, 11, 29268.
- [98] W. Qiu, P. A. Gurr, G. G. Qiao, *Macromolecules* **2020**, 53, 4090.
- [99] V. Malatesta, R. Millini, L. Montanari, *J. Am. Chem. Soc.* **1995**, 117, 6258.
- [100] V. Malatesta, F. Renzi, M. L. Wis, L. Montanari, M. Milosa, D. Scotti, *J. Org. Chem.* **1995**, 60, 5446.
- [101] J. F. Berry, *SURVICE Engineering*, Belcamp, MD **2018**.
- [102] M. Li, Q. Zhang, Y.-N. Zhou, S. Zhu, *Prog. Polym. Sci.* **2018**, 79, 26.
- [103] C. M. Kingsbury, P. A. May, D. A. Davis, S. R. White, J. S. Moore, N. R. Sottos, *J. Mater. Chem.* **2011**, 21, 8381.
- [104] C. M. Degen, P. A. May, J. S. Moore, S. R. White, N. R. Sottos, *Macromolecules* **2013**, 46, 8917.
- [105] A.-D. N. Celestine, B. A. Beiermann, P. A. May, J. S. Moore, N. R. Sottos, S. R. White, *Polymer* **2014**, 55, 4164.
- [106] H. Chen, F. Yang, Q. Chen, J. Zheng, *Adv. Mater.* **2017**, 29, 1606900.
- [107] M. Li, W. Liu, S. Zhu, *Polymer* **2017**, 112, 219.
- [108] Y. Chen, C. J. Yeh, Y. Qi, R. Long, C. Creton, *Sci. Adv.* **2020**, 6, eaaz5093.
- [109] Z. Cao, *Macromol. Chem. Phys.* **2020**, 221, 2000190.
- [110] B. A. Beiermann, D. A. Davis, S. L. B. Kramer, J. S. Moore, N. R. Sottos, S. R. White, *J. Mater. Chem.* **2011**, 21, 8443.
- [111] B. A. Beiermann, S. L. B. Kramer, J. S. Moore, S. R. White, N. R. Sottos, *ACS Macro Lett.* **2012**, 1, 163.
- [112] B. A. Beiermann, S. L. B. Kramer, P. A. May, J. S. Moore, S. R. White, N. R. Sottos, *Adv. Funct. Mater.* **2014**, 24, 1529.
- [113] P. A. May, N. F. Munaretto, M. B. Hamoy, M. J. Robb, J. S. Moore, *ACS Macro Lett.* **2016**, 5, 177.
- [114] M. E. Grady, B. A. Beiermann, J. S. Moore, N. R. Sottos, *ACS Appl. Mater. Interfaces* **2014**, 6, 5350.
- [115] L.-J. Wang, X.-J. Zhou, X.-H. Zhang, B.-Y. Du, *Macromolecules* **2015**, 49, 98.
- [116] G. L. Peterson, M. B. Larsen, M. A. Ganter, D. W. Storti, A. J. Boydston, *ACS Appl. Mater. Interfaces* **2015**, 7, 577.
- [117] N. Yenpech, V. Intasanta, K. Tashiro, S. Chirachanchai, *Polym. Chem.* **2020**, 11, 91.
- [118] G. R. Gossweiler, T. B. Kouznetsova, S. L. Craig, *J. Am. Chem. Soc.* **2015**, 137, 6148.
- [119] C. K. Lee, D. A. Davis, S. R. White, J. S. Moore, N. R. Sottos, P. V. Braun, *J. Am. Chem. Soc.* **2010**, 132, 16107.
- [120] C. K. Lee, B. A. Beiermann, M. N. Silberstein, J. Wang, J. S. Moore, N. R. Sottos, P. V. Braun, *Macromolecules* **2013**, 46, 3746.
- [121] T. A. Kim, B. A. Beiermann, S. R. White, N. R. Sottos, *ACS Macro Lett.* **2016**, 5, 1312.
- [122] X. Fang, H. Zhang, Y. Chen, Y. Lin, Y. Xu, W. Weng, *Macromolecules* **2013**, 46, 6566.
- [123] Y. Chen, H. Zhang, X. Fang, Y. Lin, Y. Xu, W. Weng, *ACS Macro Lett.* **2014**, 3, 141.
- [124] H. Zhang, Y. Chen, Y. Lin, X. Fang, Y. Xu, Y. Ruan, W. Weng, *Macromolecules* **2014**, 47, 6783.
- [125] G. Hong, H. Zhang, Y. Lin, Y. Chen, Y. Xu, W. Weng, H. Xia, *Macromolecules* **2013**, 46, 8649.
- [126] Q. Zhang, Y. Wang, C. Xing, Y. Cai, K. Xi, X. Jia, *RSC Adv.* **2017**, 7, 12682.
- [127] K.-P. Wang, Y.-P. Deng, T. Wang, Q.-D. Wang, C.-G. Qian, X.-Y. Zhang, *Polymer* **2020**, 210, 123017.
- [128] C. Xing, L. Wang, L. Xian, Y. Wang, L. Zhang, K. Xi, Q. Zhang, X. Jia, *Macromol. Chem. Phys.* **2018**, 219, 1800042.
- [129] K. Zhao, C. Lv, J. Zheng, *Sci. China: Technol. Sci.* **2020**, 63, 740.
- [130] Y. Vidavsky, S. J. Yang, B. A. Abel, I. Agami, C. E. Diesendruck, G. W. Coates, M. N. Silberstein, *J. Am. Chem. Soc.* **2019**, 141, 10060.
- [131] Q. Wang, G. R. Gossweiler, S. L. Craig, X. Zhao, *Nat. Commun.* **2014**, 5, 4899.
- [132] G. R. Gossweiler, C. L. Brown, G. B. Hewage, E. Sapiro-Gheiler, W. J. Trautman, G. W. Welshofer, S. L. Craig, *ACS Appl. Mater. Interfaces* **2015**, 7, 22431.
- [133] Y. Lin, M. H. Barbee, C. C. Chang, S. L. Craig, *J. Am. Chem. Soc.* **2018**, 140, 15969.
- [134] E. Epstein, T. A. Kim, R. H. Kollarigowda, N. R. Sottos, P. V. Braun, *Chem. Mater.* **2020**, 32, 3869.
- [135] T. Wang, N. Zhang, Y. Ge, C. Wang, Z. Hang, Z. Zhang, *Macromol. Chem. Phys.* **2019**, 221, 1900463.

- [136] L. Wang, W. Zhou, Q. Tang, H. Yang, Q. Zhou, X. Zhang, *Polymers* **2018**, 10, 994.
- [137] L.-J. Wang, K.-X. Yang, Q. Zhou, H.-Y. Yang, J.-Q. He, X.-Y. Zhang, *Chin. J. Polym. Sci.* **2020**, 38, 24.
- [138] C.-H. Wu, C.-W. Tu, J. Aimi, J. Zhang, T. Chen, C.-C. Wang, C.-F. Huang, *Polym. Chem.* **2020**, 11, 6423.
- [139] G. Kim, V. M. Lau, A. J. Halmes, M. L. Oelze, J. S. Moore, K. C. Li, *Proc. Natl. Acad. Sci. U. S. A.* **2019**, 116, 10214.
- [140] B. A. Versaw, M. E. McFadden, C. C. Husic, M. J. Robb, *Chem. Sci.* **2020**, 11, 4525.
- [141] T. Kosuge, X. Zhu, V. M. Lau, D. Aoki, T. J. Martinez, J. S. Moore, H. Otsuka, *J. Am. Chem. Soc.* **2019**, 141, 1898.
- [142] Y. Pan, H. Zhang, P. Xu, Y. Tian, C. Wang, S. Xiang, W. Weng, R. Boulatov, *Angew. Chem., Int. Ed.* **2020**, 59, 21980.
- [143] R. Colaco, S. Shree, L. Siebert, C. Appiah, M. Dowds, S. Schultzke, R. Adelung, A. Staubitz, *ACS Appl. Polym. Mater.* **2020**, 2, 2055.
- [144] M. Frenette, C. Aliaga, E. Font-Sanchis, J. Scaiano, *Org. Lett.* **2004**, 6, 2579.
- [145] J. Scaiano, A. Martin, G. P. Yap, K. Ingold, *Org. Lett.* **2000**, 2, 899.
- [146] E. Font-Sanchis, C. Aliaga, K.-S. Focsaneanu, J. Scaiano, *Chem. Commun.* **2002**, 1576.
- [147] E. Font-Sanchis, C. Aliaga, E. V. Bejan, R. Cornejo, J. Scaiano, *J. Org. Chem.* **2003**, 68, 3199.
- [148] M. Frenette, P. D. MacLean, L. R. C. Barclay, J. C. Scaiano, *J. Am. Chem. Soc.* **2006**, 128, 16432.
- [149] Y. Du, J. Chang, J. Reiner, K. Zhao, *J. Org. Chem.* **2008**, 73, 2007.
- [150] T. Watabe, K. Ishizuki, D. Aoki, H. Otsuka, *Chem. Commun.* **2019**, 55, 6831.
- [151] Y. Lu, D. Aoki, J. Sawada, T. Kosuge, H. Sogawa, H. Otsuka, T. Takata, *Chem. Commun.* **2020**, 56, 3361.
- [152] H. Oka, K. Imato, T. Sato, T. Ohishi, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2016**, 5, 1124.
- [153] F. Hoshino, T. Kosuge, D. Aoki, H. Otsuka, *Mater. Chem. Front.* **2019**, 3, 2681.
- [154] Y. Mao, Y. Kubota, T. Kurose, A. Ishigami, K. Seshimo, D. Aoki, H. Otsuka, H. Ito, *Macromolecules* **2020**, 53, 9313.
- [155] S. Kato, D. Aoki, K. Oikawa, K. Tsuchiya, K. Numata, H. Otsuka, *ACS Macro Lett.* **2021**, 10, 623.
- [156] L. S. Shannahan, Y. Lin, J. F. Berry, M. H. Barbee, M. Fermen-Coker, S. L. Craig, *Macromol. Rapid Commun.* **2020**, 42, 2000449.
- [157] C. K. Lee, C. E. Diesendruck, E. Lu, A. N. Pickett, P. A. May, J. S. Moore, P. V. Braun, *Macromolecules* **2014**, 47, 2690.
- [158] M. Li, L. Lei, Q. Zhang, S. Zhu, *Macromol. Rapid Commun.* **2016**, 37, 957.
- [159] T. Yamamoto, S. Kato, D. Aoki, H. Otsuka, *Angew. Chem., Int. Ed.* **2021**, 60, 2680.
- [160] T. Yamamoto, D. Aoki, H. Otsuka, *ACS Macro Lett.* **2021**, 10, 744.
- [161] S. Kato, S. Furukawa, D. Aoki, R. Goseki, K. Oikawa, K. Tsuchiya, N. Shimada, A. Maruyama, K. Numata, H. Otsuka, *Nat. Commun.* **2021**, 12, 126.
- [162] T. A. Kim, M. J. Robb, J. S. Moore, S. R. White, N. R. Sottos, *Macromolecules* **2018**, 51, 9177.
- [163] H. Qian, N. S. Purwanto, D. G. Ivanoff, A. J. Halmes, N. R. Sottos, J. S. Moore, *Chem* **2021**, 7, 1080.
- [164] S. Cho, S. Kang, A. Pandya, R. Shanker, Z. Khan, Y. Lee, J. Park, S. L. Craig, H. Ko, *ACS Nano* **2017**, 11, 4346.
- [165] J. Park, Y. Lee, M. H. Barbee, S. Cho, S. Cho, R. Shanker, J. Kim, J. Myoung, M. P. Kim, C. Baig, S. L. Craig, H. Ko, *Adv. Mater.* **2019**, 31, 1808148.
- [166] Y. Sheng, J. Leszczynski, A. A. Garcia, R. Rosario, D. Gust, J. Springer, *J. Phys. Chem. B* **2004**, 108, 16233.
- [167] J. Kida, D. Aoki, H. Otsuka, *Aggregate* **2021**, 2, e50.
- [168] T. Q. Nguyen, H.-H. J. M. S. Kausch, *Adv. Polym. Sci.* **1992**, 100, 73.
- [169] P. A. May, J. S. Moore, *Chem. Soc. Rev.* **2013**, 42, 7497.
- [170] Z. S. Kean, G. R. Gossweiler, T. B. Kouznetsova, G. B. Hewage, S. L. Craig, *Chem. Commun.* **2015**, 51, 9157.
- [171] T. Watabe, D. Aoki, H. Otsuka, *Macromolecules* **2021**, 54, 1725.
- [172] G. Li, L. Wang, H. Ni, C. U. Pittman, *J. Inorg. Organomet. Polym.* **2001**, 11, 123.
- [173] S. H. Phillips, T. S. Haddad, S. J. Tomczak, *Curr. Opin. Solid State Mater. Sci.* **2004**, 8, 21.
- [174] B. Janowski, K. Pielichowski, *Thermochim. Acta* **2008**, 478, 51.
- [175] T. A. Kim, C. Lamuta, H. Kim, C. Leal, N. R. Sottos, *Adv. Sci.* **2020**, 7, 1903464.
- [176] Y. Zhang, B. Ren, F. Yang, Y. Cai, H. Chen, T. Wang, Z. Feng, J. Tang, J. Xu, J. Zheng, *J. Mater. Chem. C* **2018**, 6, 11536.
- [177] H. Sakai, D. Aoki, K. Seshimo, K. Mayumi, S. Nishitsuji, T. Kurose, H. Ito, H. Otsuka, *ACS Macro Lett.* **2020**, 9, 1108.
- [178] J. Y. Jo, H. G. Jang, Y. C. Jung, D. C. Lee, J. Kim, *ACS Macro Lett.* **2019**, 8, 882.
- [179] D. W. Kim, G. A. Medvedev, J. M. Caruthers, J. Y. Jo, Y.-Y. Won, J. Kim, *Macromolecules* **2020**, 53, 7954.
- [180] J. J. Schwartz, R. Behrou, B. Cao, M. Bassford, A. Mendible, C. Shafer, A. J. Boydston, N. Boechler, *Polym. Chem.* **2020**, 11, 1122.
- [181] Y. Lee, J. Park, A. Choe, S. Cho, J. Kim, H. Ko, *Adv. Funct. Mater.* **2019**, 30, 1904523.
- [182] Z. Xia, V. D. Alphonse, D. B. Trigg, T. P. Harrigan, J. M. Paulson, Q. T. Luong, E. P. Lloyd, M. H. Barbee, S. L. Craig, *Molecules* **2019**, 24, 542.
- [183] T. Magrini, D. Kiebal, D. Grimm, A. Nelson, S. Schrettl, F. Bouville, C. Weder, A. R. Studart, *ACS Appl. Mater. Interfaces* **2021**, 13, 27481.
- [184] M. Li, W. Liu, Q. Zhang, S. Zhu, *ACS Appl. Mater. Interfaces* **2017**, 9, 15156.
- [185] D. Espalin, D. W. Muse, E. MacDonald, R. B. Wicker, *Int. J. Adv. Manuf. Technol.* **2014**, 72, 963.
- [186] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Menguc, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* **2014**, 26, 6307.
- [187] C. Schubert, M. C. van Langeveld, L. A. Donoso, *Br. J. Ophthalmol.* **2014**, 98, 159.
- [188] M. Nadgorny, A. Ameli, *ACS Appl. Mater. Interfaces* **2018**, 10, 17489.
- [189] R. T. Shafranek, S. C. Millik, P. T. Smith, C.-U. Lee, A. J. Boydston, A. Nelson, *Prog. Polym. Sci.* **2019**, 93, 36.
- [190] R. C. Rohde, A. Basu, L. B. Okello, M. H. Barbee, Y. Zhang, O. D. Velev, A. Nelson, S. L. Craig, *Polym. Chem.* **2019**, 10, 5985.
- [191] S. Roh, D. P. Parekh, B. Bharti, S. D. Stoyanov, O. D. Velev, *Adv. Mater.* **2017**, 29, 1701554.
- [192] T. Guo, X. Chen, M. Song, B. Zhang, *J. Appl. Polym.* **2006**, 100, 1824.
- [193] J. M. Ramos-Fernández, I. Beleña, M. D. Romero-Sánchez, M. Fuen-santa, C. Guillem, Á. M. López-Buendía, *Prog. Org. Coat.* **2012**, 75, 86.
- [194] J. Jiu, K. Suganuma, *IEEE Trans. Compon., Packag., Manuf. Technol.* **2016**, 6, 1733.
- [195] A. G. N. Sofiah, M. Samykano, K. Kadirgama, R. V. Mohan, N. A. C. Lah, *Appl. Mater. Today* **2018**, 11, 320.
- [196] W. Qiu, C. Zhang, G. Chen, H. Zhu, Q. Zhang, S. Zhu, *ACS Appl. Mater. Interfaces* **2021**, 13, 26490.
- [197] M. Wu, Z. Guo, W. He, W. Yuan, Y. Chen, *Chem. Sci.* **2021**, 12, 1245.
- [198] K. Yanada, S. Kato, D. Aoki, K. Mikami, H. Sugita, H. Otsuka, *Chem. Commun.* **2021**, 57, 2899.
- [199] K. Ishizuki, D. Aoki, H. Otsuka, *Macromol. Rapid Commun.* **2020**, 42, 2000429.
- [200] T. Wang, H. Wang, L. Shen, N. Zhang, *Polym. Chem.* **2021**, 12, 3832.
- [201] K. Seshimo, H. Sakai, T. Watabe, D. Aoki, H. Sugita, K. Mikami, Y. Mao, A. Ishigami, S. Nishitsuji, T. Kurose, H. Ito, H. Otsuka, *Angew. Chem., Int. Ed.* **2021**, 60, 8406.
- [202] Z. Liu, T. Liu, Q. Lin, C. Bao, L. Zhu, *Angew. Chem.* **2015**, 127, 176.
- [203] S. Kato, D. Aoki, H. Otsuka, *ACS Appl. Polym. Mater.* **2021**, 3, 594.
- [204] J. M. Clough, J. Gucht, T. E. Kodger, J. Sprakel, *Adv. Funct. Mater.* **2020**, 30, 2002716.



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