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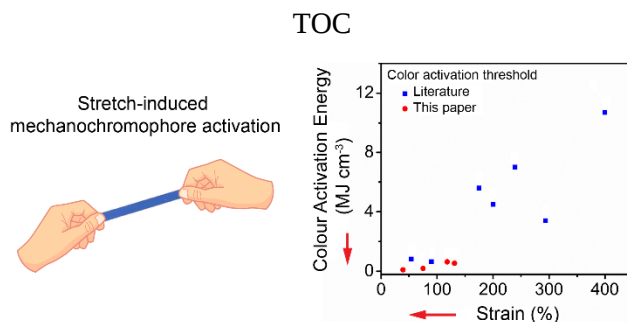
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Regulating Color Activation Energy of Mechanophore-linked Multi-network Elastomers

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ABSTRACT: To lower color activation stress/strain with remaining excellent mechanical properties for mechanochromic materials has been a challenge. Here, a structure of multi-network polyacrylates was adopted to incorporate a widely studied mechanophore, spiropyran (SP), to investigate the regulation of mechanochromic sensitivity by varying network compositions. In situ color channel intensity analysis was used to characterize deformation-induced ring-opening of SP to merocyanine (MC) for color changes. The multi-network strategy could substantially reduce the onset of mechanochromic activation strain and stress, and the resulted double-networks and triple-networks exhibited remarkable mechanochromic performance with excellent mechanical properties. The network formation conditions, including solvent ratio and type of monomers, were shown great impact on regulating the mechanochromic activities. A triple-network sample

achieved the lowest macroscopic colour activation energy compared to previously reported SP-linked elastomers. In addition, the ratio of SP to MC conversion activated by stretching was firstly shown higher than that by UV light.

1. Introduction

Stimuli-responsive materials which undergo optical change have attracted intensive studies in recent years due to their great potential in sensor applications.¹⁻³ Mechanochromic materials are one of the widely studied categories, and one of the strategies for preparation is to chemically conjugate mechanophores into polymer matrices.^{4, 5} Mechanochromic compounds which are triggered because of a chemical structure change, fall into two main categories, either based on isomerization or radical formation mechanisms.^{6, 7} Isomerisation-based mechanophores include spiropyran, spirothiopyran, rhodamine and naphthopyran, which all contain a spiro-junction that undergoes ring-opening under force, to give a resonance structure with a change in color.⁸⁻¹¹ Mechanophores based on radical formation are less reported, with diarylbibenzofuranone being one such example.^{12, 13} Among the developed mechanophores, spiropyran (SP) is the most studied one which undergoes a ring-opening reaction to form a purple colored merocyanine (MC) isomer. SP has been incorporated into a variety of polymers, including polyacrylates, polyurethane (PU), and polydimethylsiloxane (PDMS).¹⁴⁻¹⁷ In these examples, most are in the form of linear polymers or simple networks, relying on the intrinsic elasticity of the materials to transfer an applied force to the mechanophores. Examples which aimed to utilize increased intermolecular forces through hydrogen bonding and led to improved strength of the polymers, were achieved with the introduction of ureidopyrimidinone moieties along a PU backbone.^{18, 19} However, these modified SP-PU still required a large onset of activation strain (400–500%) for color change. A low

activation strain and stress are essential to make such mechanochromic elastomers useful in practical applications. Relying on simple polymeric structures to enhance the mechanical properties has been a major challenge in achieving low strain/stress activation. Additionally, the ratio of colorless SP converting to ring-opened MC induced by force has been reported significantly lower than that activated by UV light, indicating a low efficiency of SP as a mechanophore.^{15, 20} Improving the equilibrium towards the colored ring-opened MC isomer when triggered by force needs to be improved, given that the synthesis of cross-linkable SP molecules is not facile. Therefore, more advanced polymer architectures may provide new pathways to improve the mechanochromic sensitivity (low strain/stress) and efficiency of SP transforming to MC.

Double-network (DN) hydrogels have been well known for their distinct mechanical properties which exhibit tough and extendible properties despite their large water content.^{21, 22} As chain alignment and SP orientation are crucial to the mechanical activation of SP to MC,²³ pre-stretching the polymer chain with the mechanophores chemically linked will be a strategy to reduce the threshold of activation. To achieve this, the first-network needs to be rigid and brittle in order to dissipate mechanical energy, while the second-network is required to be ductile allowing for a large deformation. This contrasting nature of the first and second networks results in the fascinating mechanical properties exhibited by DN hydrogels. However, this principle was initially limited to hydrogels for over a decade since their invention, and was not translated to solvent-free elastomers due to the low swelling capability of neutral polymers.²⁴ In 2014, the Creton group successfully applied the DN principles to develop multi-network polyacrylate elastomers, which exhibited excellent mechanical properties.²⁵ When the first-network polyacrylate was swollen in acrylate monomers followed by polymerization of the second-network, a pre-stretched first-

network was formed. A triple-network obtained by one more swelling-curing step further achieved a higher strength and an earlier stress hardening region.²⁵ This multi-network elastomer is ideal for incorporation of mechanophores in the pre-stretched first-network to improve the efficiency of mechanophore conversion, and rhodamine as a mechanochromophore has been shown to undergo multi-fluorescence color-switching when conjugated in such systems.¹⁰ We propose that the spiropyran covalently linked in the first network of such a multi-network elastomer may also result in a tunable activation threshold with improved mechanochromic efficiency and good mechanical properties. SP is also much widely used and presents three different colors switching at visible range under different loading conditions.^{16, 26} In addition, unlike the mechanochromophore rhodamine, SP is multi-responsive to both UV light as well as force in color change, providing greater applicability.

Herein, we synthesized double- and triple-network polyacrylates with SP crosslinked in the first-network to investigate their mechanochromic performance. For a better representation of the activation threshold, the activation energy of color change (U_A) considering both stress and strain was introduced, which was determined by calculating area underneath the onset of color change on stress-strain curve. The influences of SP concentration, solvent volume in preparation of first-network, and types of monomer in the second-network on the mechanochromic activation were examined. A comparison of SP activation by stretching and UV irradiation was also conducted to investigate any advantages of employing a DN architecture for SP mechanical activation. Cyclic tensile tests were performed to study their mechanochromic reversibility. Through a comparison of U_A , we found that the newly designed elastomers adopting multi-network structure can regulate the mechanochromic activation energy by varying the network compositions and achieves the lowest activation energy for SP-linked elastomers ever reported.

2. Experimental Section

Materials

Butyl acrylate (BA, 99%, Sigma), methyl acrylate (MA, 99%, Sigma) and 1,4-butanediol dimethacrylate (BDMA, 95%, Sigma) were passed through basic aluminium oxide to remove the inhibitor monomethyl ether hydroquinone prior to use. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPOs, 97%, Sigma) was used as received. Toluene (AR grade) and petroleum ether (bp. 40 – 60 °C, AR grade) were used as received. Tri-methacrylate spiropyran was synthesized according to our previous work.^{26, 27}

Preparation of first-network. The concentration of crosslinkers (based on total methyl acrylate groups of SP and BDMA) were fixed at 3.5 mol % relative to monomer BA. As an example, for sample BA_{0.5} (0.5 mol % SP), SP (10.3 mg, 0.0174 mmol, 0.005 equiv), BDMA (7.71 μ L, 0.0349 mmol, 0.01 equiv), photo initiator BAPOs (5.83 mg, 0.0140 mmol, 0.004 equiv), BA (0.5 mL, 3.49 mmol, 1 equiv), and toluene (0.5 mL) were mixed thoroughly in a vial under argon. The homogeneous solution was injected into a glass mould (width:1.6 cm, length 5-5.5 cm, thickness: 0.4-0.5mm) with a silicone spacer sandwiched by two glass sheets, which was subsequently exposed to white light (4W cool white light, 350 lumens) for 2 hr for polymerization. Once cured, the samples were removed from the mould and soaked in a solution of petroleum ether (50 vol %) and toluene (50 vol %) for two days, with regular changing of the solvent, to remove any unreacted species. The swollen samples were then dried *in vacuo* to a constant mass. Samples BA_{0.83} and BA_{1.17} (0.83 mol % and 1.17 mol % of SP), were prepared in the same method varying the recipes accordingly. For the samples prepared with 40% and 60% toluene, the concentrations of SP were fixed at 0.83 mol % and the volume ratios of BA to toluene were changed to 6:4 and 4:6, respectively. Single networks (SN) were prepared at SP concentration of 0.8 wt % relative to butyl

acrylate. This SP weight content was comparable to that in DN sample $\text{BA}_{0.83}\text{BA}$ prepared with 50% toluene. Two SNs were prepared, in the presence of toluene (BA_T) and without toluene (BA_0).

Preparation of double-network. The dried first-network samples were swollen in excess volume of solution containing monomer BA (1 equiv), crosslinker BDMA (0.02 mol % equiv) and photo initiator BAPOs (0.4 mol % equiv) to a constant mass, which typically took 5 – 6 hr. The swollen samples were removed from the solution, sandwiched between two glass sheets and sealed within petri dishes to avoid oxygen and evaporation. They were then exposed to white light for 2 hr for polymerization affording double-network specimens. The specimens were soaked in mixed solvent of petroleum ether and toluene for two days, with regular changing of the solvent, to remove any unreacted species. The swollen samples were dried under vacuum until a constant mass. These DN elastomers were denoted by BABA, specifically $\text{BA}_{0.5}\text{BA}$, $\text{BA}_{0.83}\text{BA}$, $\text{BA}_{1.17}\text{BA}$ for different SP concentration in the first-network. For a different polyacrylate as a second-network, a $\text{BA}_{0.83}$ sample was swollen in a solution of monomer MA (1 equiv), crosslinker BDMA (0.02 mol % equiv) and photo initiator BAPOs (0.4 mol % equiv) to a constant mass; and then repeated as before. This sample was denoted by $\text{BA}_{0.83}\text{MA}$.

Preparation of triple-network. Triple-network samples were obtained by repeating the swelling-curing process with $\text{BA}_{0.83}\text{BA}$ and $\text{BA}_{0.83}\text{MA}$. The specimens were labelled as $\text{BA}_{0.83}\text{BABA}$ and $\text{BA}_{0.83}\text{MAMA}$, respectively.

Unreacted species in the bulk samples were quantified to be less than 3 wt % determined by mass change before and after solvent wash. UV-Vis analysis of the extracted solvents showed that no detectable signals in the visible range were observed, indicating that the mechanophores were conjugated within the crosslinked polymer networks.

Characterization

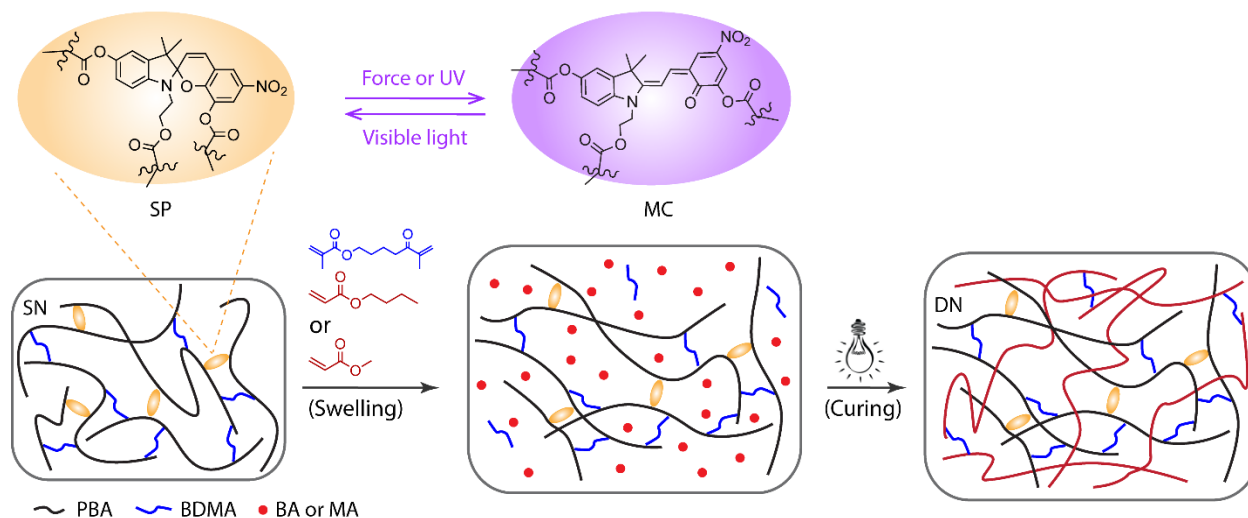
Tensile tests were performed uniaxially at room temperature on an Instron 5944 Microtester with Bluehill material testing software using a 2 kN loading cell. Dog-bone shaped specimens (gauge length: 15 mm, gauge width: 4 mm, total length: 50 mm) were used for tensile measurements cut from the obtained films using a cutting die. Tensile measurements were performed on the specimens fastened between two grips and tested in duplicate or triplicate at a strain rate of 0.5 mm s⁻¹ (Figure S1). Engineering stress and ratio of displacement are used to plot the stress-strain curves. Video recording was performed during testing for color analysis. The color change was quantified by RGB color intensity analysis. RGB values were determined after white balance calibration in Adobe PhotoshopTM software. The blue color channel ratio was determined as: $rBc = \text{Blue}/(\text{Red} + \text{Green} + \text{Blue})$, and the same calculation method was used for red and green color channel ratios, rRc and rGc , respectively. The onset strain of color activation was determined as the intersection of two tangent lines on the curves of rBc against tensile strain. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin Elmer DSC 8500 with a heating rate of 10 °C min⁻¹. T_g values were determined by the midpoint of the transition range (Figure S2). Absorbance spectra were obtained on a Shimadzu UV-Vis Scanning Spectrophotometer (UV-2101 PC) with a fast scanning rate of 1 nm intervals.

The pre-stretched ratios of first network in the final elastomers, $\lambda_{\text{prestretch}}$, were calculated by the equation of $h_{\text{DN}}/h_{\text{SN}}$ ($h_{\text{TN}}/h_{\text{SN}}$), where h_{SN} , h_{DN} and h_{TN} represents the thickness of the single (first), double and triple-network samples respectively. The swollen ratios of the first-network in the double-network or triple-network λ_{swollen} were calculated as either $m_{\text{DN}}/m_{\text{SN}}$ or $m_{\text{TN}}/m_{\text{SN}}$ respectively, where m_{SN} , m_{DN} and m_{TN} represent the mass of the single (first), double and triple-network.

3. Results and discussion

3.1 Materials and Synthesis

A trifunctional spiropyran with methyl acrylate groups (SP) was synthesized according to our previous work.²⁷ Trifunctional SP was employed due to its increased chain-aligning ability under swelling, afforded by more cross-linkable points on the molecule.^{27, 28} SP was incorporated into single network (SN) via free radical polymerization initiated by white light. The SP-based SN was using butyl acrylate (BA) as a monomer and toluene as a solvent. Unreacted BA and toluene were removed prior to fabrication of the second-network. The SN was then swollen in acrylate monomers (BA or MA) followed by photo polymerization to form double-network (DN) (Scheme 1); here the first-network was pre-stretched during the second-network formation, which facilitated chain alignment and orientation of SP mechanophores. A triple-network (TN) was obtained by a repeated swelling-curing process with a DN. As chain transfer is inevitable during radical polymerization, there could be covalent bonds between the networks.²⁹



Scheme 1. First-network SP-poly(butyl acrylate) samples were swollen in a solution of acrylate monomer and co-crosslinker, followed by white light polymerization to afford DN elastomers. SP

converts to MC under external stimuli, either by force or UV irradiation, and the process is reversible upon relaxation or exposure to visible light.

DN hydrogels with good mechanical properties typically consist of a rigid first-network and a ductile second-network.^{21, 30} Here, for elastomers, this approach was adopted and double-network polyacrylates were achieved with a high cross-link density in the first-network and a low cross-link density in the second-network. For the preparation, the pre-stretched first network was formed by swelling in the monomer solution followed by polymerization of the second network. As such, a series of SP based DN elastomers were prepared by varying the SP concentration, toluene volume in the first-network and the type of acrylate used in the second-network (denoted by BABA or BAMA), to study how the network compositions influence their mechanochromic behaviour. Two SNs, prepared with toluene solvent (BA_T) and without toluene (BA₀), and two TNs (BA_{0.83}BABA and BA_{0.83}MAMA) were also prepared for a comparison with the DN. The compositions of the elastomers, pre-stretched and swollen ratio of the first-network are summarized in Table S1. RGB color intensity analysis was employed to characterize the color change during the mechanical test to achieve dynamic measurements. The mechanical properties and mechanochromic performance of the elastomers are summarized in Table 1.

Table 1. Mechanical properties of the prepared elastomers: T_g , ultimate strength σ_{break} , strain at break ϵ_{break} , onset of color activation strain ϵ_{MC} , onset of color activation stress σ_{MC} and color activation energy U_A

Sample	T_g (°C)	σ_{break} (MPa)	ϵ_{break} (%)	ϵ_{MC} (%)	σ_{MC} (MPa)	U_A (MJ m ⁻³)
BA ₀	-44.6 ± 0.47	0.57 ± 0.07	86 ± 6	/	/	/
BA _T	-44.9 ± 0.10	0.24 ± 0.02	143 ± 17	/	/	/
BA _{0.5} BA	-46.9 ± 0.15	7.95 ± 0.18	347 ± 11	158 ± 1.1	1.39 ± 0.17	0.63 ± 0.08

BA _{0.83} BA	-46.4 ± 0.30	7.57 ± 1.14	335 ± 39	159 ± 1.6	1.40 ± 0.05	0.71 ± 0.06
BA _{1.17} BA	-46.6 ± 0.25	7.25 ± 0.62	328 ± 25	156 ± 2.8	1.40 ± 0.21	0.60 ± 0.03
BA _{0.83(40)} BA	-46.7 ± 0.46	8.04 ± 0.81	278 ± 14	131 ± 3.7	1.30 ± 0.18	0.54 ± 0.07
BA _{0.83(60)} BA	-47.5 ± 0.20	6.04 ± 0.30	397 ± 27	189 ± 12.5	1.38 ± 0.18	0.71 ± 0.13
BA _{0.83} MA	10.5 ± 1.49	8.55 ± 0.31	471 ± 64	118 ± 4.4	1.11 ± 0.03	0.63 ± 0.04
BA _{0.83} BABA	-47.9 ± 0.23	/	/	75 ± 3.8	0.81 ± 0.14	0.19 ± 0.03
BA _{0.83} MAMA	-8.9 ± 0.71	/	/	39 ± 1.4	0.72 ± 0.02	0.10 ± 0.02

3.2 Mechanochromic properties of SN vs DN

Poly(butylacrylate) is an elastomer with a low glass transition temperature (T_g), thus it behaves as an elastic polymer at room temperature. The T_g measured for the prepared samples from DSC are summarized in Table 1. Interestingly, although the mechanical properties of the DNs were better than SNs, the T_g for DNs were lower than SNs (comparing the BA series). This is attributed to the swelling-curing process endowing the DN with more free volume for the polymer chains. A further decreased T_g was detected for TN (more significant for BA_{0.83}MA and BA_{0.83}MAMA), suggesting that a greater free volume was achieved by TN structure.

SN samples BA_T and BA₀, and DN sample BA_{0.83}BA with similar SP weight contents, were compared for their elasticity and mechanochromic performance. The ultimate tensile strength (σ_{break}) and stretchability (ϵ_{break}) of BA_T and BA₀ were determined to be 0.24 ± 0.02 MPa at $143 \pm 17\%$ and 0.57 ± 0.07 MPa at $86 \pm 6\%$, respectively, which were much weaker than those of the BA_{0.83}BA with 7.57 ± 1.14 MPa at $335 \pm 39\%$ (Table 1 and Figure 1A). Neither of the SNs exhibited a strain-hardening characteristic on the stress-strain curves. As expected, BA_T was weaker than BA₀ but with larger elongation, indicating a looser network was formed in the presence of solvent. The stress-strain curve of DN presented two regions, including a softening

region due to the uncoiling of polymer chains and a hardening region due to stretching of the bonds.³¹ The DN BA_{0.83}BA exhibited a significant color change from light yellow to blue during tensile tests, whereas the SNs did not show any color change prior to fracture (Figure 1C). It demonstrated that the SN samples BA_T and BA₀ crosslinked via white light polymerization are soft and brittle, with the applied force unable to transform SP into its colored ring-opened counterpart. In contrast by performing a subsequent swelling-curing process to build a second-network, the mechanical properties are greatly improved enabling a sufficient mechanical activation of SP thus inducing a significant color change prior to breaking. The improved elasticity of BA_{0.83}BA is due to the first-network acting as a filler which can dissipate energy and enhance the elasticity.²⁹ The color change was analysed based on RGB value, and the ratio of color channel intensities were calculated. The change of blue color ratio (rBc) was more significant than rRc and rGc (Figure S3), thus rBc was used to analyse the color activation. The onset of color activation strain (ϵ_{MC}) for BA_{0.83}BA occurred at $\sim 159 \pm 1.6\%$, at the early stage of the hardening region (Figure 1B). This is consistent with the phenomena observed in SP-PDMS and PU reported previously.^{16, 32} The ϵ_{MC} of BA_{0.83}BA was significantly lower than the reported elastomers in simple structure, such as 259% for SP-PMA and 400% for SP-PU.^{19, 33} The reason for this is due to SP being in the first-network which was pre-stretched by the second-network thus shortening the deformation for chain alignment and mechanophore orientation. The onset of color activation stress (σ_{MC}) then can be determined from the stress-strain curve at the position of ϵ_{MC} . For a better description of the color activation threshold, the term of color activation energy (U_A) was introduced and it is determined by the area underneath σ_{MC} - ϵ_{MC} on the stress-strain curve (Figure 1B). It represents the amount of energy per unit volume that the elastomer needs to absorb for inducing the color change.

The calculated U_A for $BA_{0.83}BA$ is 0.71 ± 0.06 MJ m⁻³, and the U_A of all the samples are summarized in Table 1.

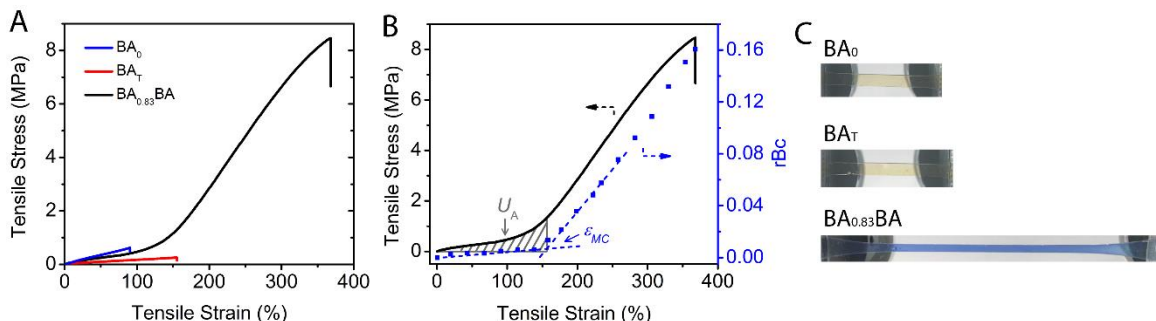


Figure 1. (A) Tensile stress-strain curves of SNs prepared in the presence/absence of toluene (BA_T and BA_0) and DN ($BA_{0.83}BA$). (B) A plot of rBc as a function of tensile strain for $BA_{0.83}BA$ with ϵ_{MC} determined by the intersection of two tangent lines. The color activation energy U_A is calculated by integration of the area underneath the onset of color change on stress-strain curve. (C) Images of the two SNs and DN $BA_{0.83}BA$ under tension prior to fracture.

3.3 Effect of varying network compositions

The concentration of SP in the first-network was varied to study its effect on their mechanochromic properties and the U_A . The cross-link density was fixed at a constant value by varying the proportion of co-crosslinker BDMA. DNs with SP concentrations of 0.5, 0.83 and 1.17 mol % relative to BA were prepared and denoted by $BA_{0.5}BA$, $BA_{0.83}BA$ and $BA_{1.17}BA$, respectively. The stress-strain curves of the three samples are shown in Figure 2A, with similar ϵ_{break} at ca. 340% and σ_{break} at 7.2–7.9 MPa (Table 1), indicating that the mechanical properties of the three samples were almost identical. It demonstrated that the elasticity of DN is dependent on the crosslinking density, and the variation of the low SP concentration had insignificant effect on the mechanical properties. The T_g for the three samples were the same within standard error. The curves of rBc

against the strain showed that the ε_{MC} was $158 \pm 1.1\%$, $159 \pm 1.6\%$ and $156 \pm 2.8\%$ for $BA_{0.5}BA$, $BA_{0.83}BA$ and $BA_{1.17}BA$, respectively (Figure 2B), which were at the strain-hardening regions. The minor differences of ε_{MC} for the DNPs with various SP concentrations revealed that ε_{MC} was reliant on the onset of stress-hardening. With increasing tensile strain, rBc exhibited a linear growth, indicating that more and more SP converted to ring-open MC. The higher SP concentration, the greater slope was observed, indicating a faster color deepening rate. Thus, at a certain strain above ε_{MC} , $BA_{1.17}BA$ presented the highest rBc. The images of the three samples under a strain around 330% exhibited a blue color with $BA_{1.17}BA$ showing the deepest color (Figure 2C). Overall, the amount of SP to MC conversion linearly increased with increasing the SP concentration in the first-network under a given deformation above activation strain (Figure 2D). The U_A calculated for $BA_{0.5}BA$, $BA_{0.83}BA$ and $BA_{1.17}BA$ are 0.63 ± 0.08 , 0.71 ± 0.06 and 0.60 ± 0.03 MJ m⁻³ (Table 1).

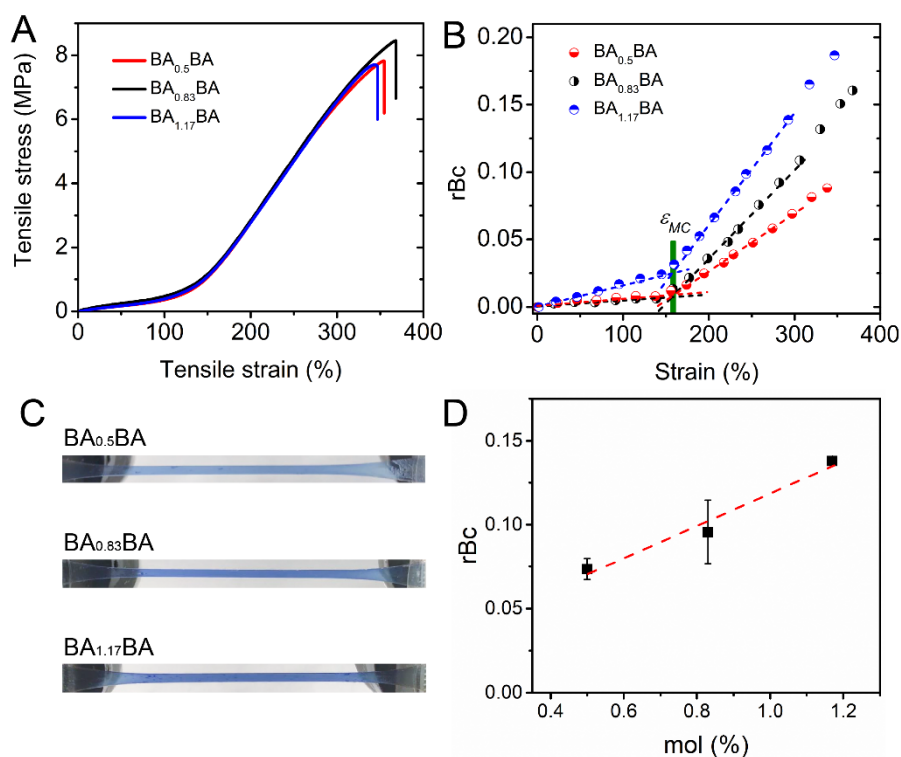


Figure 2. (A) Tensile stress-strain curves of DN samples with SP concentration of 0.5, 0.83, 1.17 mol % in the first-network. (B) Color change plots of rBc against strain for the three samples, and the onset strain of color activation ε_{MC} determined by the intersection of the two tangent lines. (C) Images of the three samples under tensile at a strain of 338%, 330% and 332%, respectively. (D) A linear relationship of SP concentration with colour intensity under a stain of 300% in the three DN samples ($R^2 = 0.995$).

The first-network acted as a filler to improve the elasticity of the subsequent DN, which could be affected by the pre-stretched ratio and swelling ability of the first-network.²⁹ By varying the toluene volume in the first-network, the pre-stretched ratio ($\lambda_{\text{prestretch}}$) and swelling ratio (λ_{swollen}) can be tuned. Three DN samples of BABA with toluene volume at 40, 50 and 60 vol % were prepared. The λ_{swollen} determined by mass ratio for the three samples were 3.84 ± 0.42 , 4.57 ± 0.03 and 5.34 ± 0.10 , respectively (Table S1), demonstrating that an increase of the solvent volume would lead to an increase of λ_{swollen} due to a looser SN formation after solvent removal. The T_g was slightly reduced with increasing toluene volume, which was attributed to the increased λ_{swollen} resulting in more free volume. The tensile stress-strain curves showed that the decrease of solvent volume caused a relatively early strain-hardening region, but at an expense of $\varepsilon_{\text{break}}$ (Figure 3A). The rBc-strain curves shown in Figure 3B displayed that the ε_{MC} differed for the three samples due to the differences of onset of strain hardening region, with ε_{MC} at $131 \pm 3.7\%$, $159 \pm 1.6\%$ and $189 \pm 12.5\%$ for samples prepared with 40%, 50% and 60% toluene volume. Accordingly, the U_A of $BA_{0.83(40)}BA$ significantly lower than the other two samples (Table 1). Under a specific strain, i.e., 290% (the maximum extensibility of $BA_{0.83(40)}BA$), the colour intensity exhibited a linear decrease with increasing the solvent volume (Figure 3C). It revealed that the color activation of the DN system was tunable by adjusting the solvent volume when prepare the first-network.

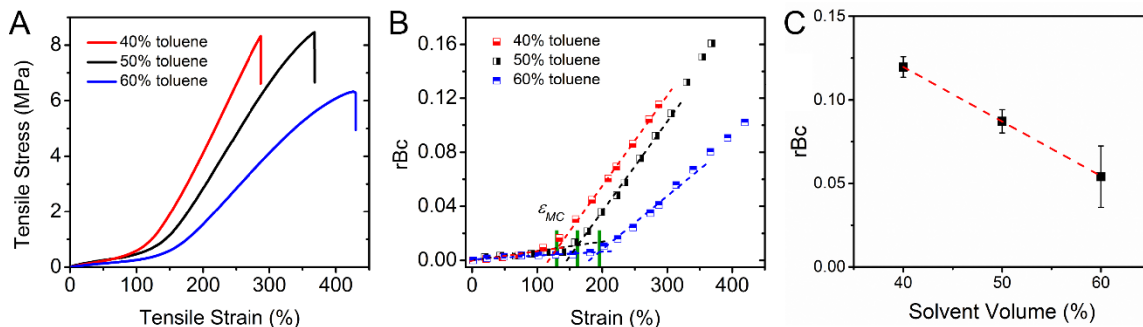


Figure 3. (A) Tensile stress-strain curves of DN samples prepared with various toluene volume in the first-network, 40%, 50% and 60%, respectively (SP concentration: 0.83 mol %). (B) Color change curves of rBc against strain for the three samples, and the onset of color activation strain ϵ_{MC} indicated by green lines. (C) A linear relationship of toluene volume with colour intensity under a strain of 290% in the three DN samples ($R^2 = 0.999$).

The elasticity of elastomers is usually related to their T_g as different polyacrylates with different T_g usually exhibit various mechanical properties. Here, since the color activation of SP is elasticity dependent, a higher T_g monomer, methyl acrylate (MA) was also employed to prepare a second-network to study the effect of network composition. The $\lambda_{swollen}$ of first-network in MA was 5.80 ± 0.29 , which was higher than that in BA with 4.57 ± 0.03 (Table S1). This could be due to the viscosity of MA lower than BA. The T_g determined by DSC for $BA_{0.83}BA$ and $BA_{0.83}MA$ were -46.4 °C and 10.5 °C, respectively (Table 1). It suggests that the T_g in DN systems were mainly determined by the material of the second-network, since its proportion is dominant in the DN samples. Both samples were in rubber state at room temperature, endowing them stretchability. The ϵ_{MC} for $BA_{0.83}BA$ at $159 \pm 1.6\%$ was significantly higher than that for $BA_{0.83}MA$ at $118 \pm 4.4\%$ (Figure 4) due to an earlier strain-hardening for $BA_{0.83}MA$, and the stress at ϵ_{MC} was 1.4 MPa for $BA_{0.83}BA$ and 1.1 MPa for $BA_{0.83}MA$; thus, the U_A of the two samples were 0.71 ± 0.06 and 0.63 ± 0.04 MJ m⁻³, respectively. The ϵ_{break} for $BA_{0.83}MA$ is higher than that for $BA_{0.83}BA$, and the

improvement of extensibility for BA_{0.83}MA was likely due to a bigger contrast between the first- and second-network and a higher λ_{swollen} , according to the design principles of DN hydrogels.³⁰ Noticeably, the first-network was the same for both DN systems, meaning that the final SP weight content in BA_{0.83}MA was lower than that in BA_{0.83}BA as a result of a higher λ_{swollen} value for BA_{0.83}MA; but the rBc of BA_{0.83}MA prior to rupture was higher than that of BA_{0.83}BA, indicating an improved mechanochromic efficiency of SP in BAMA. The results demonstrate that tunable mechanochromic sensitivity can be achieved by varying the monomer types for the networks.

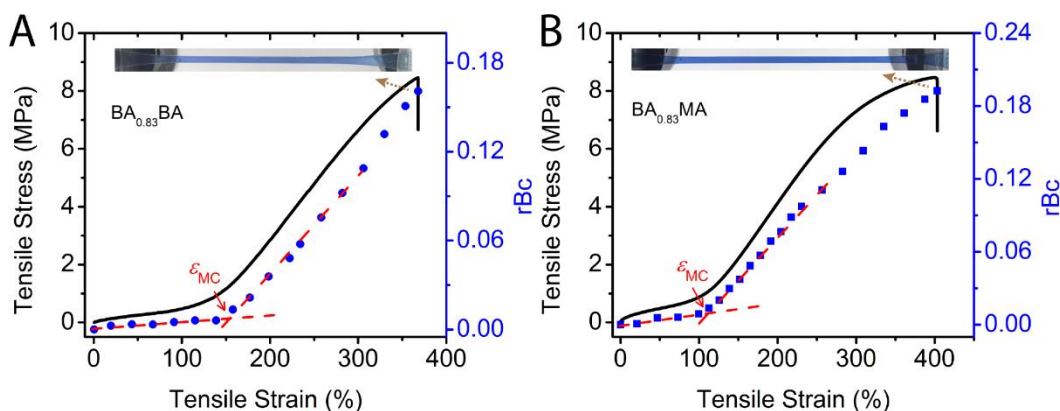


Figure 4. Tensile stress-strain curves and color change plot of rBc against strain for (A) BA_{0.83}BA and (B) BA_{0.83}MA. The onset of color activation ϵ_{MC} are indicated by the arrows. Inset pictures show a blue color when the samples were under stretching prior to fracture.

3.4 Cyclic loading-unloading tests

Cyclic tensile testing was performed on a dog-bone shaped sample of BA_{0.83}BA under a maximum strain of 250% (above ϵ_{MC}) with a strain rate of 0.5 mm s⁻¹ until rupture. A significant hysteresis loop was observed for the first cycle, and the dissipated energy was determined to be ca. 1.65 MJ m⁻³ (Figure 5A). The dissipated energy decreased remarkably after the first loading-unloading cycle and continued to drop slightly in the subsequent cycles (inset figures in Figure 5A). The

residue of strain for the 1st cycle was ca. 45% and increased to 62% after 8 times of stretching. The maximum stress of the specimen gradually dropped in the following cycles. The images of the specimen under 250% strain for the cycle of 1, 3, 5 and 7 showed that the blue color visually weakened, and it can also be seen from the quantitative analysis of rBc, which decreased continuously with increasing loading-unloading cycles (Figure 5B). As MC reverted to SP under room light, the decline of rBc was not surprising. An additional step-cyclic test was conducted with MC returning to SP forced by room light for each cycle. The sample was repeatedly stretched to a certain strain before further elongated. The plot of normalized absorbance intensity versus cycles suggested that the intensity dropped significantly with repeating the same elongation (dashed lines in Figure 5C), consistent with the trend of dissipated energy. This irreversibility of color activation is attributed to the mechanical hysteresis and the bond breakage occurring in the first-network under a certain strain,^{25, 34} which could result in the SPs located in those fragments losing their mechanochromic function once the ring-closing reaction occurs. This differs to the observation reported by Weng *et al.*, where SP in PU showed no loss of color intensity after multiple cyclic stretching.¹⁹ Besides, the sample further stretched to a larger deformation displayed a pronounced absorbance intensity again, meaning that more bonds with SP linkers were stretched.

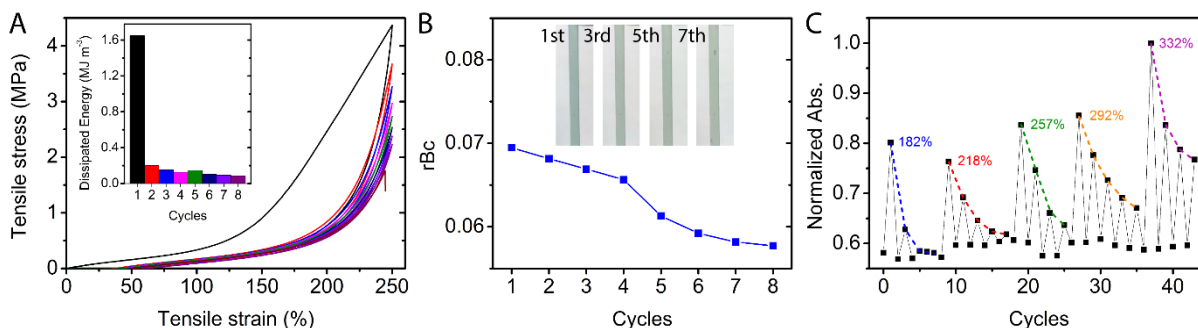


Figure 5. Cyclic tensile test on a specimen of BA_{0.83}BA until rupture. (A) Loading-unloading curves obtained at a strain rate of 0.5mm s⁻¹ and the dissipated energy for each cycle in the inset

figure. (B) The rBc value as a function of loading-unloading cycles and the inset images of the sample under a strain of 250% for the 1st, 3rd, 5th, and 7th cycle, without MC returning to SP upon relaxation for each cycle. (C) A plot of normalized absorbance intensity against loading-unloading cycles, with MC recovering to SP under exposure to room light for 30-40 min for each cycle. The sample was subjected to a specific strain for 4-5 times before further increasing the elongation, and the numbers show the value of strain corresponding to each dashed line.

3.5 Mechanical Activation vs UV Light Activation

The ratio of SP to MC conversion induced by force has been reported much lower than that by UV light, i.e. around 30% intensity for PU bearing SP, indicating a low efficiency of SP as mechanochromophore in polymers.^{15, 20} Here, the samples of BA_{0.83}BA and BA_{0.83}MA exposed to UV light were compared to those subjected to stretching to study the influence of DN structure on SP mechanical activating efficiency. The bulk samples were exposed to UV light (20 W, 365 nm) with absorption measurements performed every minute until the relative absorption intensity plateaued. Since intensity of light irradiation could affect the photo stationary state, the results obtained here were analyzed based on this specific experimental condition. The absorption peak at 580 nm attributing to MC reached a plateau after 20–30 min UV irradiation for both samples, to an absorbance intensity of 1.75 ± 0.003 and 1.27 ± 0.07 for BA_{0.83}BA and BA_{0.83}MA, respectively (Figure 6). The absorbance intensity for the stretched samples after fracture were 1.15 ± 0.03 and 1.76 ± 0.06 for BA_{0.83}BA and BA_{0.83}MA. The fraction of absorbance intensity by mechanical activation to that by UV activation was defined as $R_{F/UV}$. Based on the results, the $R_{F/UV}$ was determined to be 66% for BA_{0.83}BA and 138% for BA_{0.83}MA, and both were higher than that of those reported simple structural polymers bearing SP as mentioned earlier, which however did

not report the used UV irradiation intensity.^{15, 20} The $R_{F/UV}$ for BA_{0.83}MA over 1 highlighted that for this sample mechanical activation was greater than UV activation. To the best of our knowledge, this is the first time that mechanochromic activation has been shown to be stronger than photochromic activation for SP-based mechanochromic polymeric materials. Both the extensibility and toughness of BA_{0.83}MA contribute to the high ratio of SP to MC conversion. The high conversion proportion triggered by force proved that the DN structure elastomer bearing SP in the pre-stretched network is an effective strategy for enhancing polymer chain alignment to increase mechanical activation of the mechanophores.

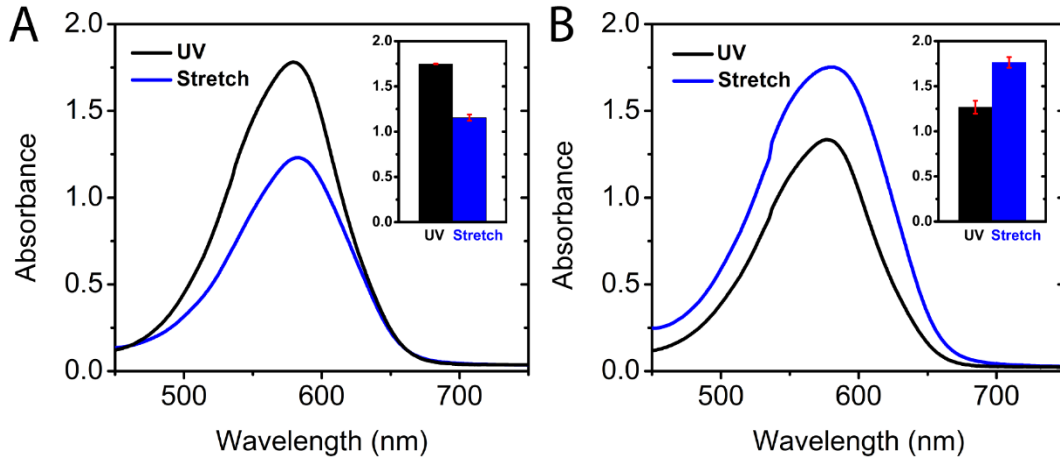


Figure 6. Absorbance spectra of (A) BA_{0.83}BA and (B) BA_{0.83}MA activated by UV light until plateaued and by stretching upon fracture. The inset figures present the absorbance intensity at the peak wavelength at 580 nm.

3.6 Triple-network and necking phenomenon

Necking phenomena for DN gels occur as a thinning zone on the sample and further grows with elongation.^{35, 36} Necking phenomenon was not observed on triple-network elastomers¹⁰ until a quadruple-network polyacrylate which was obtained through three times of swelling-curing

process.²⁹ However in this study, necking phenomenon has been observed on triple-network samples at a strain around 220% (Figure 7). Necking phenomena observed for DN hydrogels have been reported to be dependent on the structure of the first-network, i.e. cross-link density and extensibility.^{35, 37} In this case, although the cross-link density here was comparable to the reported PEA triple-network elastomer, which did not show necking,²⁹ the differences of monomer and polymerization conditions (white light initiated here) led to a dissimilar first-network, resulting in the necking phenomenon. The strain-hardening for BA_{0.83}BABA occurred at ca. 60%, resulting in a ϵ_{MC} at 75% (Figure 7B), higher than the ϵ_{MC} for BA_{0.83}MAMA sitting at $39 \pm 1.4\%$ (Figure 7D) which displayed an earlier onset of strain-hardening. The lower ϵ_{MC} of TN than that of DN was due to a further pre-stretching of the first-network. It led to the U_A of BA_{0.83}MAMA (0.10 ± 0.02 MJ m⁻³) lower than that of BA_{0.83}BABA (0.19 ± 0.03 MJ m⁻³). The low U_A equal to 0.10 MJ m⁻³ is comparable to stretching a commercially available rubber band, to a deformation of approximate 40% (Figure S4). The color intensity of BA_{0.83}MAMA was also higher than that of BA_{0.83}BABA before the occurrence of necking. Upon further stretching after ϵ_{MC} , the stress remained almost constant whereas the strain kept increasing, suggesting the occurrence of necking. The specimen displayed two regions, necked and unnecked parts (Figure 7A&C). With increasing the strain, the necked domain further elongated whereas the unnecked region gradually shortened, like “eaten” by the necked region. When the sample failed before the necked area occupied the whole gauge section, a deeper color was observed on the necked area than the unnecked domain (inset images Figure 7A&C). This could be explained by the internal fracture of the first-network leading to the necking,³⁷ and SPs were activated with the first-network expansion prior to fracture. When the sample failed with the necked area expanding to nearly the whole gauge section, the purple color was distributed along the gauge section. The shape of the DN samples can nearly fully recover

upon rupture. However, the color activation was irreversible on the necking region, due to the rupture of first-network. This uneven distribution of force/deformation on the materials upon necking would be interesting if the necking position can be controlled. According to this study and previously reported work,³⁵ the necking phenomena generally appear near the end of the gauge section. Further research work needs to be performed on this necking phenomenon on mechanochromic materials.

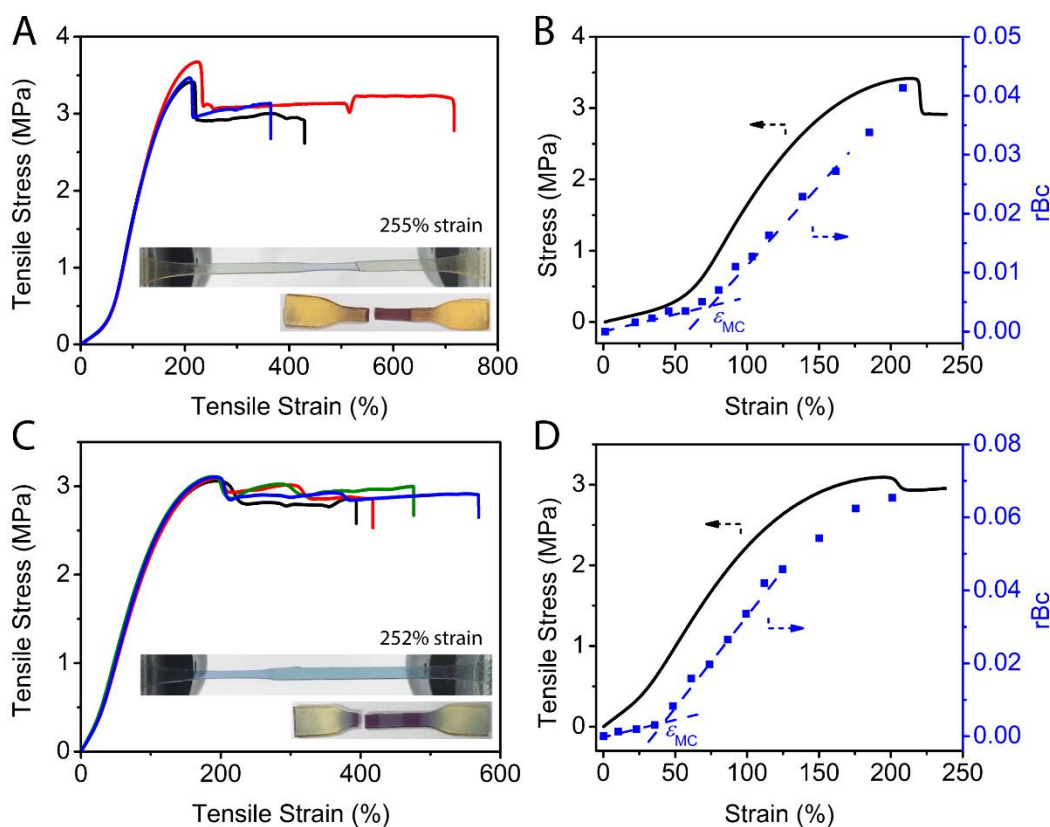


Figure 7. Stress-strain curves for (A) BA_{0.83}BABA and (B) BA_{0.83}MAMA. The inset images show the samples under necking and after failure. A stress-strain curve and a plot of rBc against strain for (C) BA_{0.83}BABA and (D) BA_{0.83}MAMA before the onset of necking phenomenon, with ϵ_{MC} determined by two tangent lines.

3.7 Comparison of mechanical activation

To evaluate the sensitivity of mechanochromic activation, the U_A of SP-linked multi-network elastomers presented in this paper are compared to the elastomers reported in the literature. It's worth noting that the mechanical testing conditions in these works are different, e.g. strain rate, which may affect their mechanochromic properties. Here, we only compare the SP-elastomers with activation threshold clearly reported and those characterized by RGB colour intensity analysis. The plot of onset of color activation stress-strain and the calculated U_A are shown in Figure 8, and the corresponding plot of U_A against strain is shown in Figure S5. Overall, the U_A of triple-network elastomer in this work is the lowest. SN of PMA bearing SP requires much larger strain and higher stress (entries 1) than the DN and TN in this work, resulting in a U_A difference in an order of magnitude. The graft copolymer PS-SP-PBA displayed an ideally low strain and stress for mechanochromic activation (entry 7), however the synthesis is tedious. Commercial PDMS (Sylgard 184) provides a facile preparation approach with an ideally low U_A , but still the TN elastomers in this work offer a lower U_A . Thus, the multi-network elastomers are excellent candidates for SP mechanochromic materials, combining the advantages of a low activation energy and a facile preparation process.

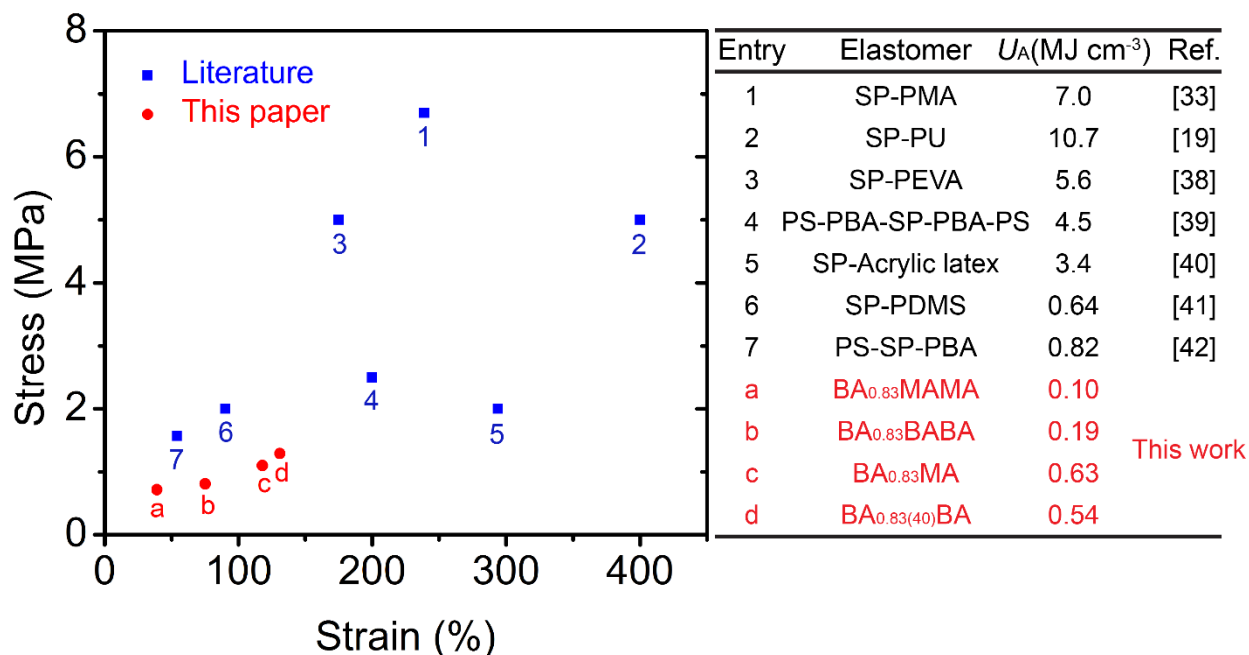


Figure 8. A plot of onset of tensile stress-strain for mechanical activation of SP-linked elastomers presented in this work (entry a-d) and reported in the literature (entry 1-7).^{19, 33, 38-42} The U_A values in the literature were calculated from reported data using methods described in this work.

4. Conclusion

In conclusion, we have adopted multi-network polyacrylates to allow SP to be pre-stretched in the first-network for regulating mechanochromic sensitivity. The results showed that the mechanochromic activation was reliant on the strain-hardening region, while the variation of SP concentration in DN samples had negligible effect on the onset strain of color activation, but the blue color intensity presented a linear growth with increasing SP concentration under a given deformation. A reduced toluene volume allowed an early appearance of onset of color activation strain at a cost of ultimate elongation and resulted in a linear increase of SP to MC conversion. A change in acrylate monomer for the second-network showed that BA_{0.83}MA displayed an advantage over BA_{0.83}BA at the mechanochromic performance. The cyclic tension test suggested

that there was a significant hysteresis loop in the first loading, and the blue color intensity gradually dropped with increasing cycle numbers. A comparison of SP to MC conversion activated by stretching and by UV irradiation demonstrated that the mechanical activation was improved remarkably than those reported simple structure polymers bearing mechano-active SP. A triple-network elastomer could further reduce the U_A , and exhibited a necking phenomenon, which could be utilized for color switchable applications required to indicate large deformations at a low stress. The comparison of U_A between this work and reported elastomers shows that the TN has the lowest U_A . The highly sensitive mechanochromic elastomers making use of the mechanical advantages from multi-network structures provide potential for the fabrication of new sensors with color response, and the regulable mechanochromic sensitivity offers more options for such sensors with a wide sensing range.

ASSOCIATED CONTENT

Supporting Information

Compositions and swelling parameters of DN and TN SP-polyacrylates, tensile stress-strain curves of DN samples, DSC curves, RGB color channel intensities plots, a plot of U_A against strain, and tensile stress-strain curves of commercially available rubber bands.

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Notes

The authors declare no competing financial interest.

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