

Wide-ranging Force Responsive Composites based on 1,2-Dioxetane and ZnS as Luminescent Probes in Polyurethanes

Jin-Hui Zhang^a, Shuang Liu^a, Yuan Yuan^{a*}, and Yu-Lan Chen^{a,b*}

^a Department of Chemistry, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300354, China

^b State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China

 Electronic Supplementary Information

Abstract Combining the advantages of mechanochemiluminescence from 1,2-dioxetane and elastico-mechanoluminescence from ZnS particles, a new kind of mechanoluminescent polymer composites are developed. They can emit bright luminescence with two distinct colors at different strains, empowering a versatile mechanochemical strategy for force sensing and damage detection at a wider force responsive range.

Keywords Mechanochemiluminescence; 1,2-Dioxetane; Elastico-mechanoluminescence; ZnS; Polymer composites

Citation: Zhang, J. H.; Liu, S.; Yuan, Y.; Chen, Y. L. Wide-ranging force responsive composites based on 1,2-dioxetane and ZnS as luminescent probes in polyurethanes. *Chinese J. Polym. Sci.* 2023, 41, 1162–1168.

INTRODUCTION

In polymer mechanochemistry, chemical transformations in polymers are facilitated using mechanical force. This burgeoning area has boosted the development of mechano-responsive polymers as stress sensing materials, whereby the macroscopic force is translated into specific outputs through the incorporation of mechano-sensitive units (mechanophores) into polymer main chains.^[1–6] A range of mechanophores with visualized mechano-responsive signals, such as color changes,^[7] fluorescence,^[8,9] phosphorescence^[10] and chemiluminescence,^[11] have been reported. Among them, bis(adamantyl)-1,2-dioxetane (**Ad**) has been demonstrated as a versatile mechanochemiluminescent mechanophore.^[12–19] When this mechanophore is covalently coupled with polymer chains or networks, the strained four-membered ring can be opened, leading to two carbonyl (typically ketone) moieties, one of which is in an electronically excited state. When the excited ketone relaxes into the ground state, blue light at wavelength of ca. 420 nm emits.^[11] Such kind of mechanochemiluminescence from polymers does not require external excitation sources and has high spatial and temporal resolution, therefore, has attracted great attention owing to its potential applications in mechanosensors.^[16,20–24] However, the mechanochemiluminescence only occur along with chain scission events, so that fairly high force threshold and visualized force detection mostly at the fracture moment are resulted. This issue limits the sensing

applications of **Ad** mechanophore. In particular, the force sensing at low strain/stress and prior to chain scission are beyond its capability.

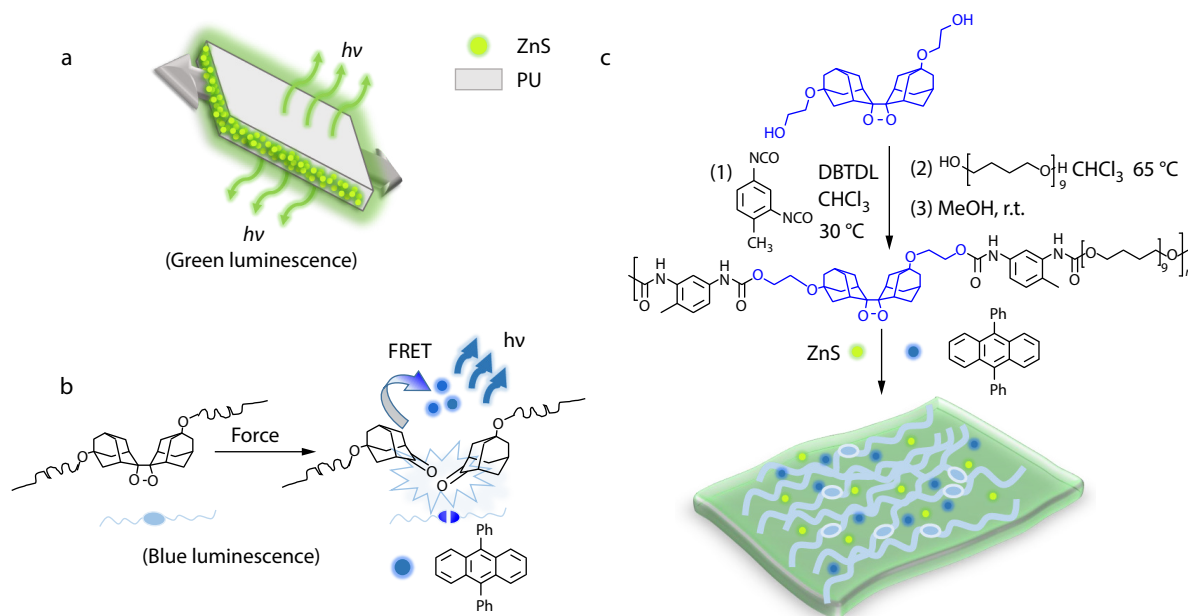
Besides the mechanochemiluminescence from covalent mechanophores, inorganic particles, such as rare-earth-ion-doped aluminates silicates and zinc sulfide (ZnS), are well known for their elastico-mechanoluminescent feature.^[25–33] When they are incorporated in flexible polymer matrix, bright light can be stimulated under elastic deformation. Taking ZnS for example, in 2015, Wang *et al.* mixed ZnS:Mn with flexible PDMS, which was laminated in transparent PET films with EVA. The resulted polymer films displayed real-time pressure feedback by luminescence photos.^[34] In 2018, Song *et al.* dispersed rigid ZnS:Mn²⁺ (Mn/Cu)/Al₂O₃ particles (ZMP) in PDMS and printed them as flexible mechanoluminescent skin-drive devices.^[35] Since the elastico-mechanoluminescence from these inorganic particles is caused by virtue of lattice defects and piezoelectric electric fields, its sensitivity can be promoted greatly, with visualized signals mainly concentrated at the very beginning of stretching process and sensitive to low strain.^[36–40]

To expand the mechano-responsive range, we herein combined the advantages of **Ad** for covalent bond scission indicator and elastic-luminescent ZnS for elastic deformation detection.^[11,29] A new kind of **Ad** containing mechanoluminescent polyurethane was synthesized with ZnS particles physically blended in the polyurethane matrix. Thus, ZnS/polyurethane composite films were obtained from solvent assistant hot pressing method. Upon deformation, green luminescent signal driven by elastic deformation of ZnS/polyurethane was observed at a low strain (Scheme 1a). Then blue mechanochemiluminescent signal was captured, resulting from the

* Corresponding authors, E-mail: yyuan@tju.edu.cn (Y.Y.)

E-mail: yulanchen@jlu.edu.cn (Y.L.C.)

Received May 13, 2023; Accepted May 31, 2023; Published online June 26, 2023



Scheme 1 (a) The elasto-mechanoluminescence of zinc sulfide (ZnS) in polymer matrix; (b) The mechanochemiluminescence of bis(adamantyl)-1,2-dioxetane (**Ad**); (c) Synthetic scheme of mechano-responsive ZnS/polyurethane composite film.

bond scission of **Ad** followed with fluorescence resonance energy transfer (FRET) process from the excited ketone to 9,10-diphenylanthracene (DPA) as acceptor (Scheme 1b).^[17,19,21] Using this strategy by combining ZnS particles and **Ad** mechanophore together, the optical force threshold of composite films was decreased, and the force responsive range was expanded. Moreover, distinct mechanoluminescent colors could be used to distinguish elastic deformation and bond scission events under tensile tests, empowering the dual-functional mechano-responsive polymers with improved sensitivity for dual-modal force reporting.

EXPERIMENTAL

Materials

Unless otherwise specified, all reagents and solvents were purchased from Sigma-Aldrich, TCI or Tianjin Jiangtian Chemical Company and used without further purification. ZnS was purchased from Zhejiang Minhui Luminous Technology Company (Type: MHG-8DY; Lot No: 201711206). Polytetrahydrofuran (PTMG; $M_n=650$ g/mol) was dried under vacuum at 70 °C for 2 h before used. Chloroform (CHCl_3) was dried by distillation with CaH_2 under argon before used. 5,5'/(2-Hydroxyethylenoxy) adamantane 1,2-dioxetane (**Ad**) with three isomers and polyurethane (PU) were prepared according to literature procedures.^[11,41] All reactions were performed under argon atmosphere unless otherwise stated, and all glassware was dried in oven prior to use.

Characterization

$^1\text{H-NMR}$ spectra were recorded in CDCl_3 solvent on a Bruker AVANCE III-400 spectrometer. Gel permeation chromatography (GPC) analysis was performed on a Shimadzu LC10-AT with polystyrene as standard and THF as an eluent at a flow rate of 1.0 mL/min. X-ray diffractometer (XRD) experiments were carried out on Rigaku SmartLab X-ray diffractometer. Field

emission scanning electron microscopy (FE-SEM) tests and energy dispersive X-ray spectroscopy (EDXS) tests were performed on a Hitachi Limited model SU800 instrument. Differential scanning calorimetry (DSC) measurements were conducted in TA Instruments Q-20 with a scan rate of 10 °C/min under nitrogen atmosphere.

Optomechanical Testing

Tensile experiments were recorded out on a TA Rheometrics, DHR-2 equipped with an Xpansion Instruments, SER3, extensional fixture. The drums of the fixture were colored black by permanent marker to eliminate reflecting light. The transparent double sided sticky tape was put on the drums to tightly fix the polymer film without slippage. The composite film has been shielded from light before uniaxial elongation tests. Mechanochemiluminescence videos and images were captured in darkness using a pco.edge 5.5 camera equipped with a Nikon AF NIKKOR 50 mm 1:1.4D lens. All of the videos were recorded under the same and optimized condition as in the rolling shutter color mode with shooting rate of 200 fps and exposure time of 4.98 ms. All frames showing luminescence were exported as separate monochrome TIF-files and light intensity was analyzed using a homemade-code implemented in MATLAB.^[17,19] The analyzed light intensity includes light emitted in the entire visible light range.

Synthesis of PU-1

Ad (64.7 mg, 0.1538 mmol) and dibutyltin dilaurate (DBTDL, 5 μL) were dissolved in dry CHCl_3 solution (2 mL) in a 100 mL two-necked flask. 2,4-Tolylene diisocyanate (TDI, 783.58 mg, 4.4992 mmol) dissolved in CHCl_3 (3 mL) was added to the flask under argon atmosphere and pre-polymerized at 30 °C for 45 min, and a solution of PTMG (2.81 g, 4.323 mmol) dissolved in CHCl_3 (15 mL) was added dropwise. The reaction was carried out at 65 °C for 6.5 h. Upon completion, the mixture was cooled to room temperature, with CH_3OH (10 mL) added to terminate the

reaction, and precipitated into stirring *n*-hexane. The *n*-hexane was decanted and the polymer was washed with fresh *n*-hexane for 3 times. The polymer was collected and dried under vacuum at room temperature to afford **PU-1** as a transparent elastomer matrix. $M_n=132$ kDa, $\bar{D}=1.9$.

Synthesis of PU-2 (Without Ad)

TDI (756.72 mg, 4.345 mmol) and DBTDL (5 μ L) were dissolved in dry CHCl_3 solution (5 mL) in a 100 mL two-necked flask. PTMG (2.81 g, 4.323 mmol) dissolved in CHCl_3 (15 mL) was added to the flask under argon atmosphere and polymerized at 65 $^{\circ}\text{C}$ for 4 h. Upon completion, the mixture was cooled to room temperature, added CH_3OH (10 mL) to terminate the reaction, and precipitated into stirring *n*-hexane. The *n*-hexane was decanted and the polymer was washed 3 times by adding fresh *n*-hexane and decanting the solvent. The polymer was collected and dried under vacuum at room temperature to afford **PU-2** as a transparent elastomer matrix. $M_n=98$ kDa, $\bar{D}=1.4$.

Preparation of ZnS/PU Composite Films

PU-1 (300 mg) and THF (3–7 mL, as little as possible) were added to a Teflon beaker and stirred until they were completely dissolved. ZnS (0–600 mg) and 9,10-diphenylanthracene (DPA, 1 mg) were added to the viscous polymer solution and fully stirred. Then the polymer blend was compressed by a tablet pressing machine at 80 $^{\circ}\text{C}$, 20 MPa for 3 min to obtain uniform composite films (**ZnS-0mg/PU-1**, **ZnS-300mg/PU-1**, **ZnS-600mg/PU-1**) with the size of $45 \times 25 \times (0.22 \pm 0.01)$ mm ($L \times W \times T$). The composite films (**ZnS-0mg/PU-2**, **ZnS-600mg/PU-2**) were prepared with similar procedure as the control samples by using **PU-2** as the matrix. The five sets of composite films were cut into rectangular sample strips with the size of 25×2.5 mm and a thickness of 0.22 ± 0.01 mm using a manual cutting device (Zwick ZCP 020) for optomechanical tests.^[41]

RESULTS AND DISCUSSION

As shown in Scheme 1(c), mechanochemiluminescent segmented polyurethane (**PU-1**) was synthesized through mild polycondensation, using polytetrahydrofuran (PTMG, $M_n=650$ g/mol) as the soft segment and 2,4-tolylene diisocyanate (TDI) as

the hard segment.^[41] Bis-hydroxyl functionalized 1,2-dioxetane (**Ad**, Fig. S1 in the electronic supplementary information, ESI) was incorporated into the polymer backbone, serving as the mechanoluminescent mechanophore. Then the composite films were prepared, with physically blended DPA as the fluorescent acceptor to improve light intensity from broken **Ad**, and the commercial available ZnS particles (the crystal structure, surface morphology and element composition of ZnS were characterized as shown in Figs. S2–S4 in ESI) as inorganic fillers to endow the composite films elastico-mechanoluminescent properties.^[19,29] Films with various contents of ZnS from 0 mg to 600 mg were obtained (**ZnS-0mg/PU-1**, **ZnS-300mg/PU-1**, **ZnS-600mg/PU-1**, Table 1). Meanwhile, polyurethanes without **Ad** (**PU-2**) were synthesized and their ZnS composite films (**ZnS-0mg/PU-2**, **ZnS-600mg/PU-2**, Table S1 in ESI) were prepared as control samples. DSC curves of all the films (Fig. S6 in ESI) demonstrated low glass transition temperature (T_g) around -35 $^{\circ}\text{C}$, corresponding to their elastic nature independent of ZnS and **Ad** contents.

Table 1 Feed ratios of ZnS/PU-1 composite films.

Entry	PU-1 (mg)	ZnS (mg)	DPA (mg)
ZnS-0mg/PU-1	300	0	1
ZnS-300mg/PU-1	300	300	1
ZnS-600mg/PU-1	300	600	1

Optomechanical properties of **ZnS/PU-1** were studied on a rheometer equipped with an Expansion Instruments SER Universal Testing Platform and a high-speed camera to record the luminescence in darkness (Videos S1–S3 in ESI). **ZnS-0mg/PU-1**, **ZnS-300mg/PU-1**, and **ZnS-600mg/PU-1** films with varied ZnS contents were compared at a Hencky strain rate of 20 s^{-1} . As shown in Fig. 1(a) and Fig. S8 (in ESI), all the films demonstrate good mechanical strength, whose fracture stress and fracture energy were almost similar to each other, except for **ZnS-600mg/PU-1** showing slightly decreased mechanical properties due to increased phase separation at high doping concentration of ZnS. Upon deformation, the **ZnS-300mg/PU-1** and **ZnS-600mg/PU-1** films show green mechanoluminescence at the very initial stage. Further

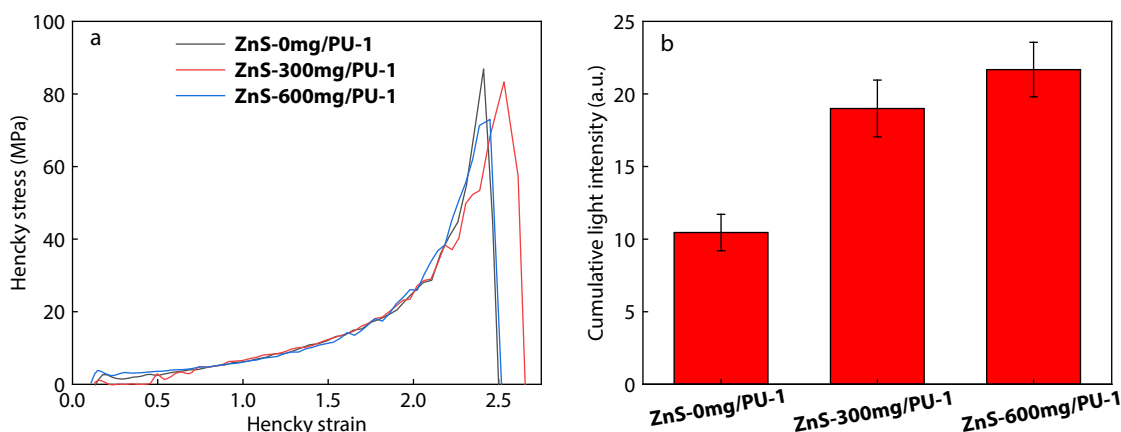


Fig. 1 (a) Representative Hencky stress-strain curves and (b) the corresponding cumulative light intensity of **ZnS-0mg/PU-1**, **ZnS-300mg/PU-1** and **ZnS-600mg/PU-1** containing 0.33 wt% DPA at Hencky strain rate of 20 s^{-1} . (Points represent average and standard deviation from three parallel experiments for each sample.)

stretching the film led to the appearance of intense blue luminescence in all the three **ZnS/PU-1** films, accompanied by a pronounced localization of mechanoluminescence at the fracture, which was in line with the activation of the **Ad** mechanophore. The cumulative light intensity of the composite films was found increasing as the ZnS content increased (Fig. 1b). Since the amount of **Ad** and the mechanical properties of the three films were similar, stronger elasto-mechanoluminescence from ZnS contributed mostly to the promoted total light intensity from **ZnS-0mg/PU-1** to **ZnS-600mg/PU-1**.

To verify the elasto-mechanoluminescent properties of the composites, the control film **ZnS-600mg/PU-2** (without **Ad**) was stretched in darkness (Video S4 in ESI). **ZnS-600mg/PU-1** and **ZnS-600mg/PU-2** possessed similar fracture stress and fracture energy, whereas the cumulative light intensity of **ZnS-600mg/PU-2** was distinctly lower than that of **ZnS-600mg/PU-1** (Fig. S9 in ESI). Unlike the dual optical signals (green and blue mechanoluminescence at different strain ranges) emitted from the deformed **ZnS-600 mg/PU-1**

film as described above, upon stretching, the **ZnS-600mg/PU-2** composite films only released green light before the strain of 145%, but with almost no light above this strain (Fig. S10 in ESI). These results indicated that the green light was originated from the elasto-mechanoluminescent nature of ZnS in polyurethane matrix. The relationship between the cumulative light intensity and strain/stress of **ZnS-600mg/PU-1** and **ZnS-600mg/PU-2** was summarized in Fig. S11 (in ESI). At the early stage of stretching, the trends of two curves were almost coincident. As the mechanical deformation continuing, **ZnS-600mg/PU-1** experienced a significant enhancement in cumulative light intensity due to the effective bond scission of 1,2-dioxetane as the dominant step for mechanical energy dissipation.

More detailed analyses of the optomechanical properties of the **ZnS/PU-1** film were performed to demonstrate its dual-modal force reporting ability at broader force range. The cumulated light intensity were plotted against the applied Hencky strain, and compared to the Hencky stress-strain curves, assuming that the highest stress corresponded to the

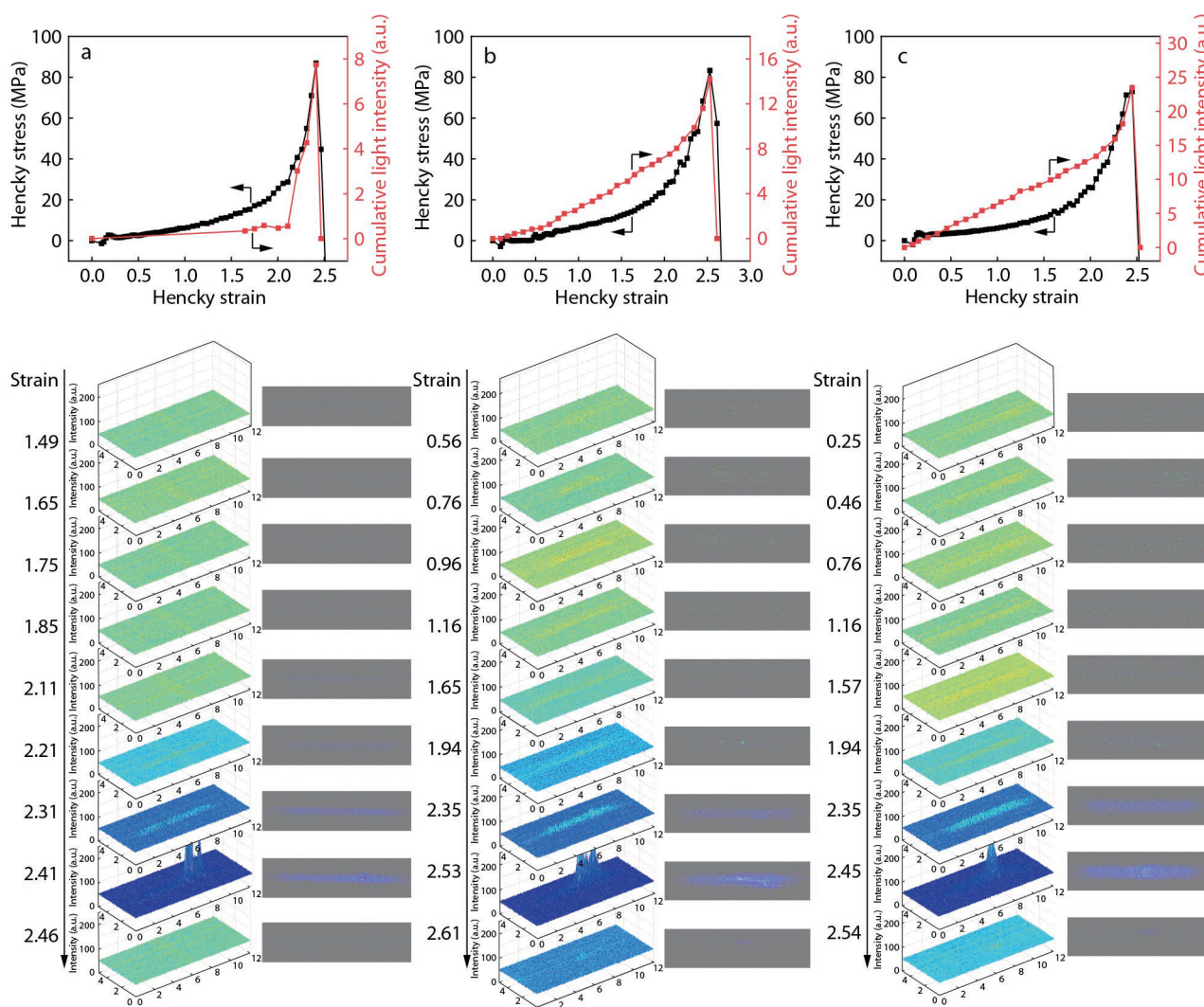


Fig. 2 Evolutions of Hencky stress and cumulative light intensity versus Hencky strain (top) and optical images (bottom) during stretching of (a) **ZnS-0mg/PU-1**, (b) **ZnS-300mg/PU-1** and (c) **ZnS-600mg/PU-1** containing 0.33 wt% DPA at Hencky strain rate of 20 s^{-1} .

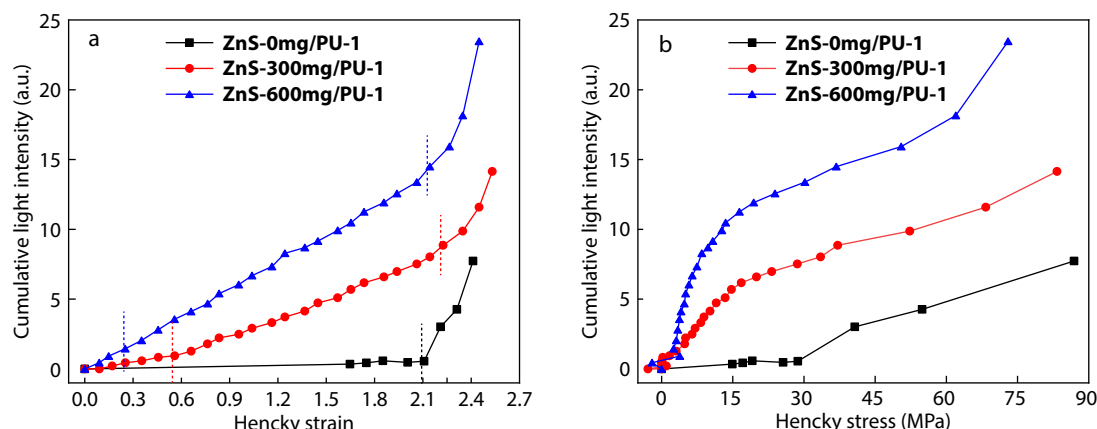


Fig. 3 Cumulative light intensity versus (a) Hencky strain and (b) Hencky stress of **ZnS-0mg/PU-1**, **ZnS-300mg/PU-1** and **ZnS-600mg/PU-1** containing 0.33 wt% DPA during stretching at Hencky strain rate of 20 s^{-1} .

film fracture (Fig. 2). First, the **ZnS-0 mg/PU-1** film (without ZnS) only emitted blue light at a high threshold, e.g., within the Hencky strain range of 200%–250%, corresponding to covalent bond scission during fracture. In contrast, the composite films of **ZnS-300mg/PU-1** and **ZnS-600mg/PU-1** exhibited dual signals with different luminescent colors: (1) at low strain, ZnS was activated firstly and green light emitted throughout the whole film, corresponding to elastic-mechanoluminescence. At this stage, the applied force was insufficient to break the covalent bond; (2) as the Hencky strain gradually increasing, blue mechanoluminescence appeared through the sample. Then, a marked increase in luminescence intensity was detected, along with a pronounced localization of scission at the fracture site. No further luminescence was observed after fracture. These results demonstrated the transient nature of the dual optical signals, allowing real time monitoring of elastic-deformation and chain-scission events with high sensitivity.

Then, the effect of ZnS content on mechanoluminescence sensitivity was summarized in Fig. 3. When the Hencky strain was lower than 2.1, the cumulative light intensity of **ZnS-300mg/PU-1** and **ZnS-600mg/PU-1** increased gradually and was almost proportional to the Hencky strain, while no light was captured from the **ZnS-0mg/PU-1** film, verifying the excellent strain sensing ability of the incorporated ZnS. Furthermore, the cumulative light intensity of all the films increased remarkably when Hencky strain reached up to 2.1 upon deformation. Similar results were illustrated in Fig. 3b, as the cumulative light intensity from **ZnS-600mg/PU-1** film increased most significantly with stress. These results revealed that the elastico-mechanoluminescence from ZnS was mostly concentrated at the Hencky strain lower than 2.1, and more intense mechanoluminescence from **Ad** began at the strain of 2.1, corresponding to the covalent bond scission. This effect is more profound for composite films with higher amount of ZnS, e.g., the strain threshold for green mechanoluminescence was determined to be 56% and 25% for **ZnS-300mg/PU-1** and **ZnS-600mg/PU-1**, respectively. These results jointly proved that the combination of elastic-mechanoluminescent ZnS and covalent mechanophore **Ad** could not only expand the visualized force responsive range, but also

improve the force reporting sensitivity, in terms of increased light intensity and enriched mechanoluminescent modal. Notably, rather than synthetic elaborations and coupling of various mechanophores, our strategy is more concise and powerful to probe the much earlier deformation process with high spatial and temporal resolution.

CONCLUSIONS

In conclusion, mechanoluminescent polyurethanes with 1,2-dioxetane as the covalent mechanophore and ZnS as the elastico-mechanoluminescent indicator were synthesized. Upon uniaxial elongation tests, these composite films displayed good mechanical properties, and emitted green and blue luminescent signals successively, indicating elastic deformation and covalent bond scission events, respectively. Taking advantages of both mechanoluminescent moieties, the limitations arose from the large force threshold for luminescence from **Ad**, as well as the weak elastico-mechanoluminescence from ZnS now can be addressed, resulting in force reporting polymers responsible at effectively expanded force range, and with appreciable and dual modal optical changes.

Conflict of Interests

Yu-Lan Chen is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-3013-4>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 22275068, 21734006,

21975178 and 21905200) and the Open Project of the State Key Laboratory of Supramolecular Structure and Materials.

REFERENCES

- Li, X. P.; Yang, F.; Li, Y. R.; Liu, C.; Zhao, P.; Cao, Y.; Xu, H. P.; Chen, Y. L. Diselenide as a dual functional mechanophore capable of stress self-reporting and self-strengthening in polyurethane elastomers. *CCS Chem.* **2023**, *5*, 925–933.
- Shen, H.; Cao, Y. Z.; Lv, M. J.; Sheng, Q. X.; Zhang, Z. B. Polymer mechanochemistry for the release of small cargoes. *Chem. Commun.* **2022**, *58*, 4813–4824.
- Sha, Y.; Zhou, Z.; Zhang, J. L.; Chen, X. F.; Luo, Z. Y.; Li, X. Heterobimetallic block copolymers with a combined main-chain/side-chain topology. *Chem. Commun.* **2023**, *59*, 207–210.
- Larsen, M. B.; Boydston, A. J. “Flex-activated” mechanophores: Using polymer mechanochemistry to direct bond bending activation. *J. Am. Chem. Soc.* **2013**, *135*, 8189–8192.
- Ramirez, A. L.; Kean, Z. S.; Orlicki, J. A.; Champhekar, M.; Elsagr, S. M.; Krause, W. E.; Craig, S. L. Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces. *Nat. Chem.* **2013**, *5*, 757–761.
- Sun, C.; Zhang, S. N.; Ren, Y. X.; Zhang, J. Y.; Shen, J. Y.; Qin, S. Y.; Hu, W.; Zhu, S. Q.; Yang, H.; Yang, D. K. Force-induced synergetic pigmentary and structural color change of liquid crystalline elastomer with nanoparticle-enhanced mechanosensitivity. *Adv. Sci.* **2022**, *9*, 2205325.
- Zhang, H.; Gao, F.; Cao, X. D.; Li, Y. Q.; Xu, Y. Z.; Weng, W. G.; Boulatov, R. Mechanochromism and mechanical-force-triggered cross-linking from a single reactive moiety incorporated into polymer chains. *Angew. Chem. Int. Ed.* **2016**, *55*, 3040–3044.
- Muramatsu, T.; Shimizu, S.; Clough, J. M.; Weder, C.; Sagara, Y. Force-induced shuttling of rotaxanes controls fluorescence resonance energy transfer in polymer hydrogels. *ACS Appl. Mater. Interfaces* **2023**, *15*, 8502–8509.
- Baumann, C.; Stratigaki, M.; Centeno, S. P.; Göstl, R. Multicolor mechanofluorophores for the quantitative detection of covalent bond scission in polymers. *Angew. Chem. Int. Ed.* **2021**, *60*, 13287–13293.
- Filonenko, G. A.; Lugger, J. A. M.; Liu, C.; van Heeswijk, E. P. A.; Hendrix, M. M. R. M.; Weber, M.; Müller, C.; Hensen, E. J. M.; Sijbesma, R. P.; Pidko, E. A. Tracking local mechanical impact in heterogeneous polymers with direct optical imaging. *Angew. Chem. Int. Ed.* **2018**, *57*, 16385–16390.
- Chen, Y. L.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. W.; Sijbesma, R. P. Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain. *Nat. Chem.* **2012**, *4*, 559–562.
- Ducrot, E.; Chen, Y. L.; Bulters, M.; Sijbesma, R. P.; Creton, C. Toughening elastomers with sacrificial bonds and watching them break. *Science* **2014**, *344*, 186–189.
- Yuan, Y.; Yuan, W.; Chen, Y. L. Recent advances in mechanoluminescent polymers. *Sci. China Mater.* **2016**, *59*, 507–520.
- Schuster, G. B.; Turro, N. J.; Steinmetzer, H. C.; Schaap, A. P.; Paler, G.; Adam, W.; Liu, J. C. Adamantylideneadamantane-1,2-dioxetane. An investigation of the chemiluminescence and decomposition kinetics of an unusually stable 1,2-dioxetane. *J. Am. Chem. Soc.* **1975**, *97*, 7110–7118.
- Meijer, E. W.; Wynberg, H. The synthesis and chemiluminescence of a stable 1,2-dioxetane. *J. Chem. Educ.* **1982**, *59*, 1071–1072.
- Yuan, Y.; Chen, Y. L. Visualized bond scission in mechanically activated polymers. *Chinese J. Polym. Sci.* **2017**, *35*, 1315–1327.
- Yuan, W.; Yuan, Y.; Yang, F.; Wu, M. J.; Chen, Y. L. Improving mechanoluminescent sensitivity of 1,2-dioxetane containing thermoplastic polyurethanes by controlling energy transfer across polymer chains. *Macromolecules* **2018**, *51*, 9019–9025.
- Yuan, Y.; Li, M. W.; Yuan, W.; Yang, F.; Chen, Y. L. Polyurethane/siloxane hybrid polymers with chemiluminescent mechanophores as stress probes. *Macromol. Mater. Eng.* **2019**, *304*, 1900056.
- Yuan, Y.; Chen, W. B.; Ma, Z.; Deng, Y. K.; Chen, Y.; Chen, Y. L.; Hu, W. P. Enhanced optomechanical properties of mechanochemiluminescent poly(methyl acrylate) composites with granulated fluorescent conjugated microporous polymer fillers. *Chem. Sci.* **2019**, *10*, 2206–2211.
- Chen, W.; Yuan, Y.; Chen, Y. L. Visualized bond scission in mechanochemiluminescent polymethyl acrylate/cellulose nanocrystals composites. *ACS Macro Lett.* **2020**, *9*, 438–442.
- Yang, F.; Yuan, Y.; Sijbesma, R. P.; Chen, Y. L. Sensitized mechanoluminescence design toward mechanically induced intense red emission from transparent polymer films. *Macromolecules* **2020**, *53*, 905–912.
- Yuan, Y.; Di, B. H.; Chen, Y. L. Mechanically induced bright luminescence from 1,2-dioxetane containing PDMS boosted by fluoroboron complex as an in-chain fluorophore. *Macromol. Rapid Commun.* **2021**, *42*, 2000575.
- Deng, Y. K.; Yuan, Y.; Chen, Y. L. Covalently cross-linked and mechanochemiluminescent polyolefins capable of self-healing and self-reporting. *CCS Chem.* **2021**, *3*, 1316–1324.
- Cao, B. H.; Chen, W.; Wei, W. Y.; Chen, Y. L.; Yuan, Y. Carbon dots intensified mechanochemiluminescence from waterborne polyurethanes as tunable force sensing materials. *Chinese J. Polym. Sci.* **2021**, *39*, 1403–1411.
- Zhang, J.; Bao, L. K.; Lou, H. Q.; Deng, J.; Chen, A.; Hu, Y. J.; Zhang, Z. T.; Sun, X. M.; Peng, H. S. Flexible and stretchable mechanoluminescent fiber and fabric. *J. Mater. Chem. C* **2017**, *5*, 8027–8032.
- Chandra, B. P.; Chandra, V. K.; Jha, P. Piezoelectrically-induced trap-depth reduction model of elastico-mechanoluminescent materials. *Physica B* **2015**, *461*, 38–48.
- Zhang, Y.; Gao, G. Y.; Chan, H. L. W.; Dai, J. Y.; Wang, Y.; Hao, J. H. Piezo-phototronic effect-induced dual-mode light and ultrasound emissions from ZnS:Mn/PMN-PT thin-film structures. *Adv. Mater.* **2012**, *24*, 1729–1735.
- Hurma, T. Structural and optical properties of nanocrystalline ZnS and ZnS:Al films. *J. Mol. Struct.* **2018**, *1161*, 279–284.
- Jeong, S. M.; Song, S.; Joo, K. I.; Kim, J.; Hwang, S. H.; Jeong, J.; Kim, H. Bright, wind-driven white mechanoluminescence from zinc sulphide microparticles embedded in a polydimethylsiloxane elastomer. *Energy Environ. Sci.* **2014**, *7*, 3338–3346.
- Sohn, K. S.; Timilsina, S.; Singh, S. P.; Lee, J. W.; Kim, J. S. A mechanoluminescent ZnS:Cu/rhodamine/SiO₂/PDMS and piezoresistive CNT/PDMS hybrid sensor: red-light emission and a standardized strain quantification. *ACS Appl. Mater. Interfaces* **2016**, *8*, 34777–34783.
- Tian, Y.; Zhang, Y. Y.; Zhang, X. Y.; Pan, H. Z.; Zhang, L. L.; Liu, S.; Chen, Y. L.; Su, L.; Zhao, P. Q.; Chang, J.; Wang, H. J. “Magnetism-optogenetic” system for wireless and highly sensitive neuromodulation. *Adv. Healthc. Mater.* **2022**, *11*, 2102023.
- Persits, N.; Aharoni, A.; Tur, M. Quantitative characterization of ZnS:Mn embedded polyurethane optical emission in three mechanoluminescent regimes. *J. Lumin.* **2017**, *181*, 467–476.
- He, B.; Sheng, H. X.; Liu, Q.; Hu, Z. F.; Wang, J. N.; Hu, X. Q.; Yang, Y.

- K.; Wang, Y.; Li, Z.; Liu, X. Q. Synergistically promoted charge separation/transfer in a ZnO nanosheet photoanode via the incorporation of multifunctional 3DrGO. *Chem. Commun.* **2022**, 58, 8622–8625.
- 34 Wang, X. D.; Zhang, H. L.; Yu, R. M.; Dong, L.; Peng, D. F.; Zhang, A. H.; Zhang, Y.; Liu, H.; Pan, C. F.; Wang, Z. L. Dynamic pressure mapping of personalized handwriting by a flexible sensor matrix based on the mechanoluminescence process. *Adv. Mater.* **2015**, 27, 2324–2331.
- 35 Qian, X.; Cai, Z. R.; Su, M.; Li, F. Y.; Fang, W.; Li, Y. D.; Zhou, X.; Li, Q. Y.; Feng, X. Q.; Li, W. B.; Hu, X. T.; Wang, X. D.; Pan, C. F.; Song, Y. L. Printable skin-driven mechanoluminescence devices via nanodoped matrix modification. *Adv. Mater.* **2018**, 30, 1800291.
- 36 Jeong, S. M.; Song, S.; Lee, S. K.; Choi, B. Mechanically driven light-generator with high durability. *Appl. Phys. Lett.* **2013**, 102, 051110.
- 37 Jeong, S. M.; Song, S.; Lee, S. K.; Ha, N. Y. Color manipulation of mechanoluminescence from stress-activated composite films. *Adv. Mater.* **2013**, 25, 6194–6200.
- 38 Sohn, K. S.; Timilsina, S.; Singh, S. P.; Choi, T.; Kim, J. S. Mechanically driven luminescence in a ZnS:Cu-PDMS composite. *APL Mater.* **2016**, 4, 106102.
- 39 Fontenot, R. S.; Allison, S. W.; Lynch, K. J.; Hollerman, W. A.; Sabri, F. Mechanical, spectral, and luminescence properties of ZnS:Mn doped PDMS. *J. Lumin.* **2016**, 170, 194–199.
- 40 Chandra, V. K.; Chandra, B. P.; Jha, P. Strong luminescence induced by elastic deformation of piezoelectric crystals. *Appl. Phys. Lett.* **2013**, 102, 241105.
- 41 Liu, S.; Yuan, Y.; Li, J. Y.; Sun, S. Q.; Chen, Y. L. An optomechanical study of mechanoluminescent elastomeric polyurethanes with different hard segments. *Polym. Chem.* **2020**, 11, 1877–1884.