Chinese Journal of Polymer Science Vol. 35, No. 11, (2017), 1315–1327

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag GmbH Germany 2017

Review

Visualized Bond Scission in Mechanically Activated Polymers*

Yuan Yuan and Yu-lan Chen**
Department of Chemistry, Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

Abstract Visualization and quantitative evaluation of covalent bond scission in polymeric materials are critical in understanding their failure mechanisms and improving the toughness and reliability of the materials. Mechano-responsive polymers with the ability of molecular-level transduction of force into chromism and luminescence have evoked major interest and experienced significant progress. In the current review, we highlight the recent achievements in covalent mechanochromic and mechanoluminescent polymers, leading to a bridge between macroscopic mechanical properties and microscopic bond scission events. After a general introduction concerning polymer mechanochemistry, various examples that illustrate the strategies of design and incorporation of functional and weak covalent bonds in polymers were presented, the mechanisms underlying the optical phenomenon were introduced and their potential applications as stress sensors were discussed. This review concludes with a comment on the opportunities and challenges of the field.

Keywords Mechanochemistry; Mechanochromic polymer; Mechanoluminescent polymer; Stress sensor

INTRODUCTION

Polymers are a great versatile class of materials which are found in many areas of our modern life. Strengthening and toughening polymer-based materials is a long-term important yet challenging topic in the field of engineering materials. However, it is inevitable that fatigue and failure are always coupled with polymer subjected to use. The microscopic defects under stress, especially at the initial stage of failure, usually do severe harm to the macroscopic properties of materials. What is already known is that the failure of a polymer by necessity starts with a molecular event and stress-induced bond scission often initiates fracture; therefore, probing these rare chemical events preceding macroscopic fracture and investigating the corresponding mechanisms at molecular level are essential for rational molecular strategies of advanced materials with improved mechanical properties. These requests, from both a fundamental and an applied standpoint, promote the research efforts on highly sensitive molecular probes for bond scission[1–4].

Polymer mechanochemistry, whereby chemical transformations in polymers are facilitated using mechanical force, is becoming a burgeoning area over the last decade[5]. Mechano-active polymers that can respond intelligently to mechanical force are attractive since they could connect the comprehensive investigations across molecular and macroscopic scales[6, 7]. When specific weak bonds are provided with polymeric substituents, polymer chains can be used as "handles" for transduction of macroscopic forces onto the

* This work was financially supported by the National Natural Science Foundation of China (Nos. 21522405 and 51503142), the Thousand Youth Talents Plan, and the Natural Science Foundation of Tianjin (No. 15JCYBJC52900).
** Corresponding author: Yu-lan Chen (陈于蓝), E-mail: yulan.chen@tju.edu.cn
Received June 27, 2017; Revised July 18, 2017; Accepted July 20, 2017
doi: 10.1007/s10118-017-2002-x

level of chemical bonds. In detail, the possibility arises to apply mechanical forces in a highly directional fashion because the stress can be transmitted to the centered weak bonds through the stretched polymer main chains, and finally, the cumulated stress quantitatively leads to selective bond scission. As a result, the recent progress on mechano-active polymers has boosted the development of stress sensing materials through the translation of macroscopic force into specific outputs[8, 9]. As an important sort of mechano-active polymers, mechanochromic and mechanoluminescent polymers provide perhaps the best opportunities for build-in stress sensor with high spatial and temporal resolutions, since the bond scissions in these polymers accompany with visual and quantitative optical signals.

This mini-review describes the recent development of mechano-active polymers for bond scission visualization, particularly focusing on the covalent mechanochromic and mechanoluminescent polymers. We begin with the discussion of mechanochromic polymers using spiropyran (SP) as the mechanophore, following with more exciting examples of ring-opening and radical-forming systems. Subsequently, mechanofluorescent and mechanochemiluminescent polymers with potential applications as stress sensors are considered. We conclude this review with advantages of mechanochromic and mechanoluminescent polymers as stress sensing materials, and perspectives of the field. Other aspects of mechano-active polymers with optical output related to the change of molecular assemblies[10] are well known and important fields, but they will not be discussed here.

MECHANOCHROMIC POLYMERS

Mechanochromic polymers display vivid color generation or changing when mechanical force is loaded along the polymer chains. Pioneering work regarding covalent polymer mechanochromism was reported by Davis and co-workers in 2009[11]. They incorporated spiropyran (SP) into the macromolecular backbones covalently, either as the center of a linear elastic polymethacrylate (PMA) or as the crosslinker of a glassy poly(methyl methacrylate) (PMMA) network. Upon deformation of these materials, the 6-π electrocyclic ring-opening of SP into the red merocyanine (MC) occurred and the color of polymer films turned from colorless to red (Fig. 1). Measuring the change in absorbance of the polymers allows for visual C—O bond scission and stress detection in a quantitative way. By far SP is the most widely studied mechanophore. Comprehensive studies on polymeric SP demonstrated that SP could be covalently linked with versatile polymers, such as polycaprolactone (PCL)[12], polyurethane (PU)[13], block copolymers[14, 15], hydrogen bonded supramolecular polymers[16, 17], robust hydrogels[18] *etc*., which could be performed as an optical stress probe in different kinds of polymers.

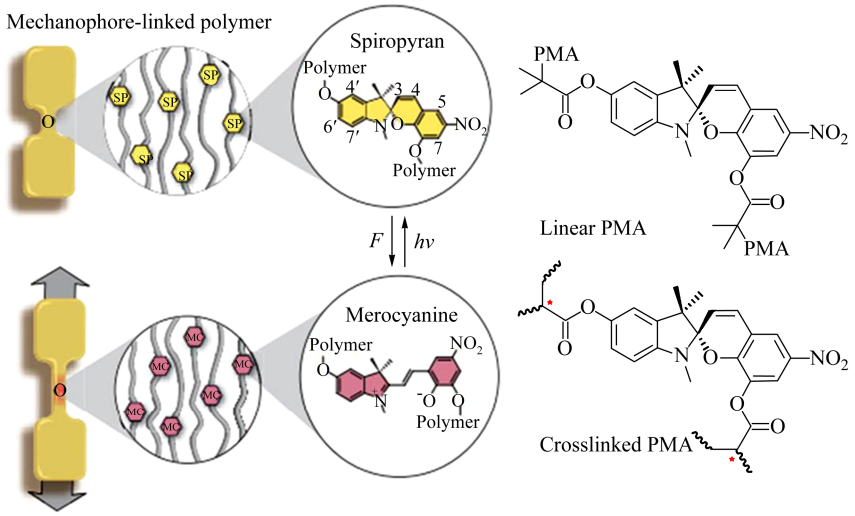


Fig. 1 Schematic representation of mechanochromism by converting polymeric spiropyran (SP) into merocyanine (MC) under mechanical force (Reprinted with permission from Ref. [11]; Copyright (2009) Nature Publishing Group)

Besides SP, several other cases of color-generating mechanophores were developed recently. Generally, they could be divided into two types, with ring-opening structures or radicals as the products under mechanical force, as listed in Fig. 2. For example, naphthopyran was found as a new regioisomer-specific mechanophore exhibiting orange-yellow color from its ring-opening product. Interestingly, the mechanochemical reactivity of naphthopyran was critically dependent on its regiochemistry. Mechanochromic behavior was only observed for its regioisomer with substitution at the 5-position, while when polymer chains were attached at the 8- and 9-positions of the naphthopyran group, the corresponding polymers were mechanically inactive. The trend in reactivity was accurately predicted by density functional theory (DFT) calculations, and the authors attributed the differences to the alignment of the target C—O pyran bond with the direction of the applied mechanical force which effected mechanochemical transduction along the reaction coordinate (Fig. 3)[19].

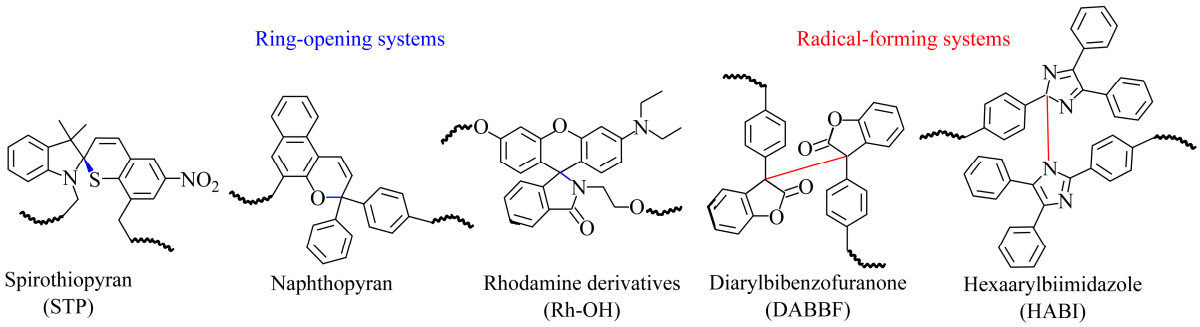


Fig. 2 Ring-opening type and radical-forming type mechanophores with mechanochromic properties in polymers (The broken bonds were drawn in color.)

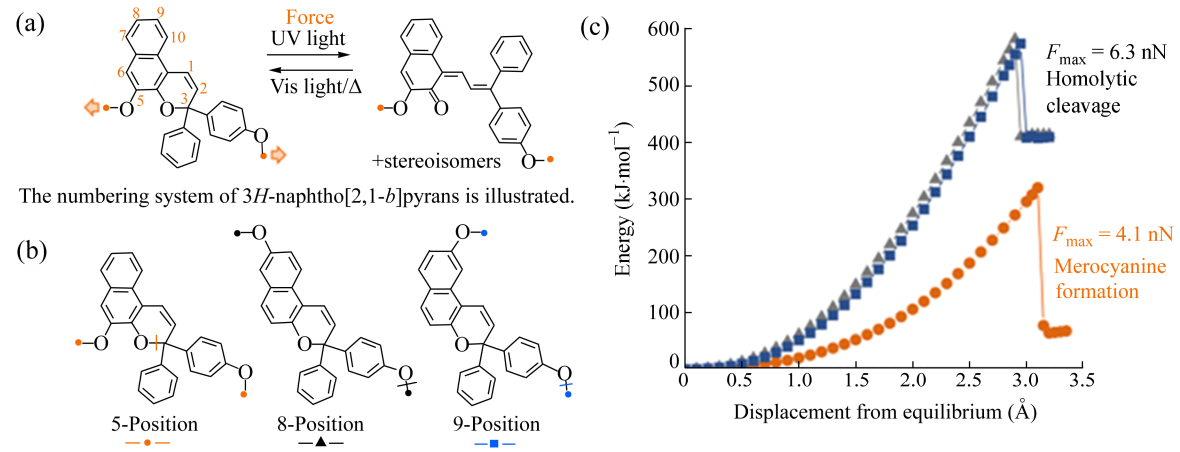


Fig. 3 (a) Transformation of 5-position substituted naphthopyran into a colored merocyanine species accomplished using mechanical force; (b) Structures of naphthopyran regioisomers substituted at different positions; (c) DFT calculations (CoGEF) for three naphthopyran regioisomers to predict regioisomer-specific mechanochemical reactivity (Reprinted with permission from Ref. [19]; Copyright (2016) American Chemical Society)

Weng *et al.* reported that polymers incorporating spirothiopyran (STP) manifest both green mechanochromism and load-induced addition reactions in solution and solid. Similar to that of SP, the chromic mechanism from the colorless STP linked polyester (PES) or polyurethane (PU) was based on the stress induced S—C bond scission to form the green colored ring-opening thiomerocyanine (TMC). Moreover, the resulted thiolate moiety was reactive and could undergo rapid thiol-ene click reactions with certain C=C bonds to form graft or crosslinked polymer (Fig. 4a). Therefore, STP was estimated as a unique mechanophore exhibiting dual mechanochemical response to report and repair bond scission in polymers[20].

Jia and co-workers selected rhodamine (Rh-OH) as another effective color producing mechanophore to synthesize polyurethane-based elastomer. DFT calculations (CoGEF) showed that the C—N bond of Rh-OH was relatively weak and the minimum energy needed for its force-induced ring-opening reaction was as low as 32 kcal·mol^{-1}. Rh-OHs were covalently linked with crosslinked polyurethane network, which showed distinct color and fluorescence changes under pressure originated from the chemical transformation of Rh-OH from a twist spirolactam into a planarized zwitterionic structure. Dual responsive chromism with reversible color switching was observed not only under mechanical force but also upon UV irradiation (Fig. 4b)[21]. Following, Bai and co-workers developed another rhodamine-based mechanochromic elastomer. Under mechanical force the elastomer showed a vibrant fluorescent color change from pale blue to red. At the same time, transformation from colorless to dark red could also be observed with naked eyes, and removal of mechanical stress led to yellow fluorescence. In this work, three-primary-color fluorescence emission stimulated by stress was realised, and reversible broad-spectrum fluorescence color change could be achieved consequently (Fig. 4c)[22].

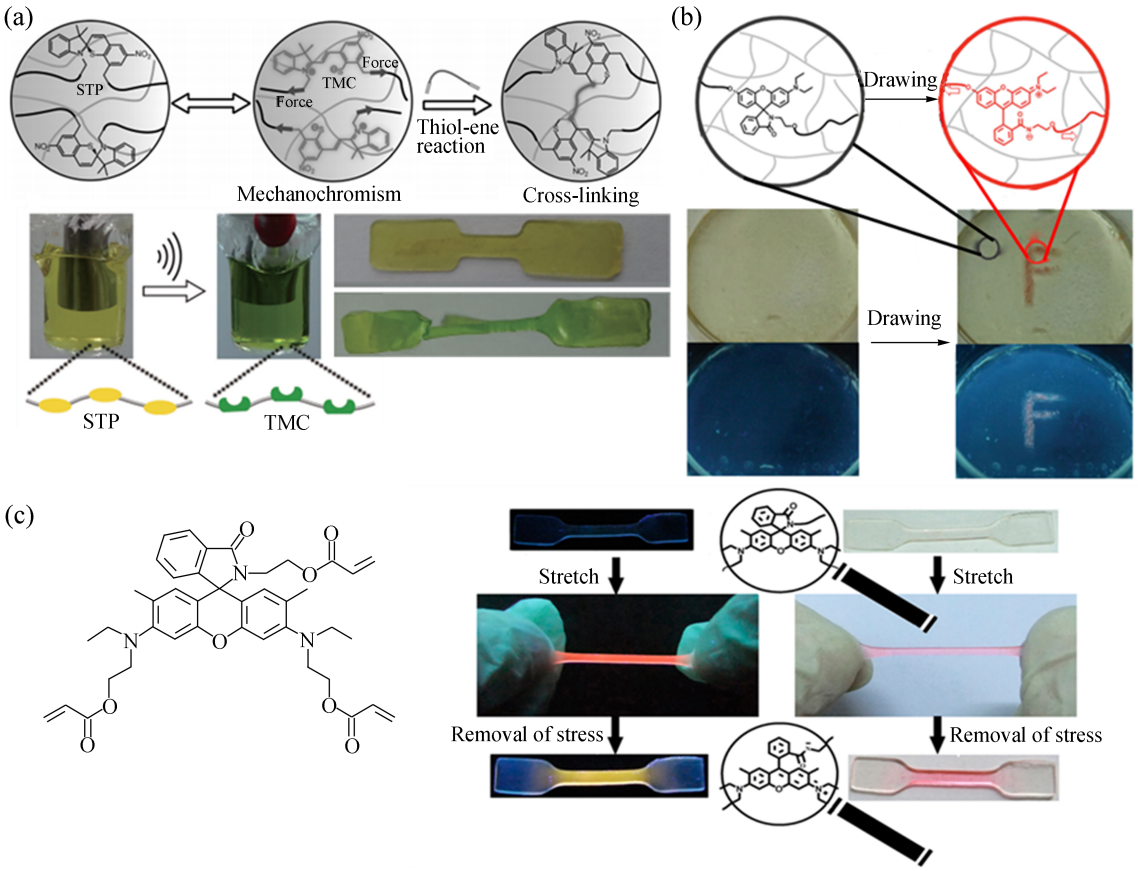


Fig. 4 (A) Schematics of dual mechanochemistry of polymeric spirothiopyran with the capacity to undergo force induced color changing and crosslinking (up) and photographs of polymer solutions under sonication and polymer films under elastic deformation (down) (Reprinted with permission from Ref. [20]; Copyright (2016) WILEY-VCH); (b) Mechano-chemical transformation of polymeric Rh-OH after drawing (Reprinted with permission from Ref. [21]; Copyright (2015) WILEY-VCH); (c) Chemical structure of Rh mechanophore (left), fluorescent (middle) and optical (right) images of manually stretched elastomer (Reprinted with permission from Ref. [22]; Copyright (2017) American Chemical Society)

In addition to the well-known ring-opening reactions, recently, polymer mechanochromism was achieved in radical-forming systems as well. The first case was described by Otsuka *et al.* in 2015 by using diarylbibenzofuranone (DABBF) derivatives as color-changing mechanophores (Fig. 5a). DABBF could act as the covalent crosslinker in polyurethane to form polymer gels in 1,4-dioxane. Freezing the gels induced force

along polymer chains and concomitant radicals by homolytic cleavage of DABBF (Fig. 5b). The radicals are blue-colored and show greatly reduced reactivity toward oxygen. Because of these distinctive properties, this radical system enabled *in situ* quantitative evaluation of polymer chain scission and mechanical energy generated along polymer chains through electron paramagnetic resonance (EPR) studies[23].

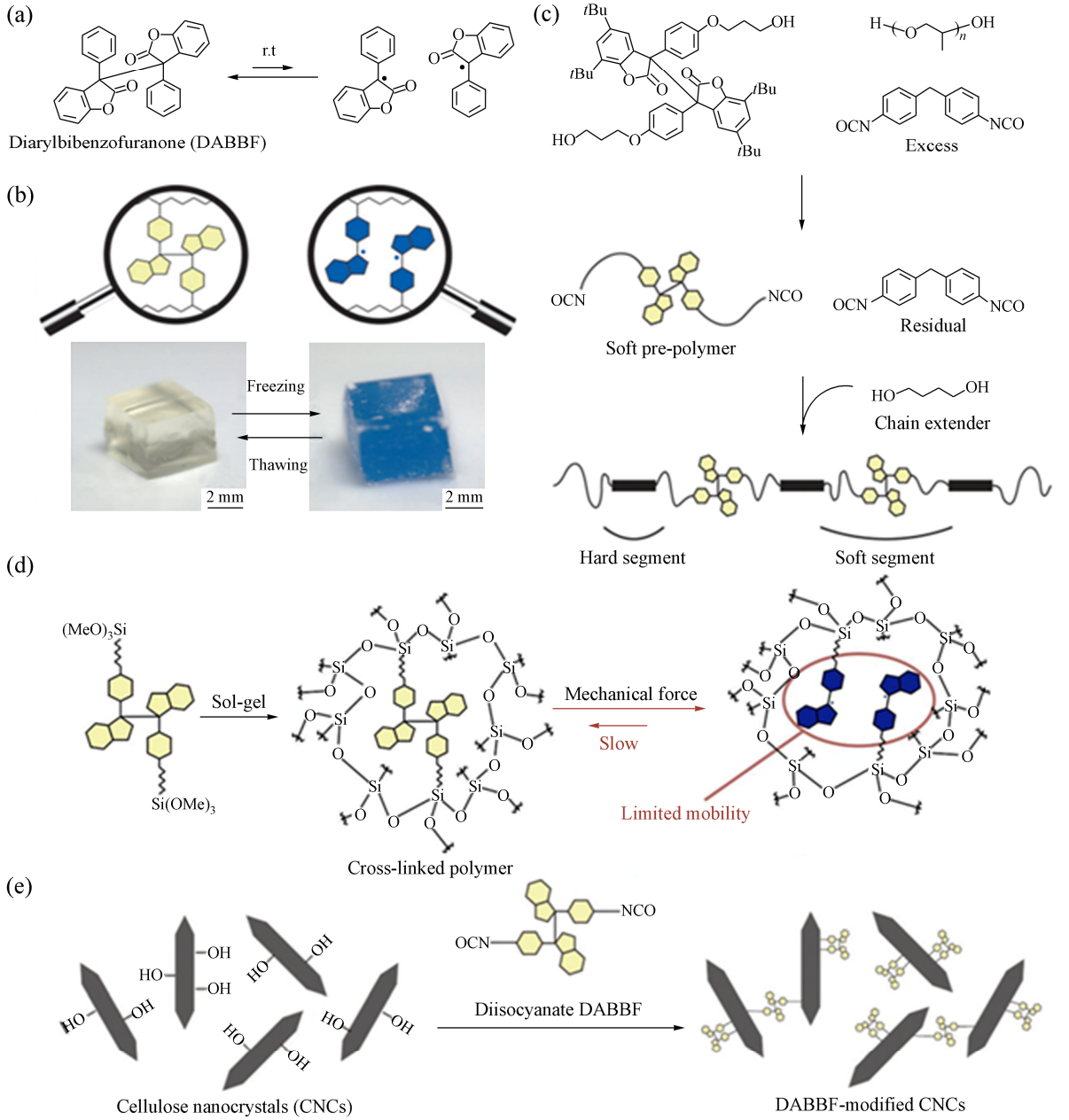


Fig. 5 (a) Equilibrium between DABBF and its corresponding blue-coloured radicals and (b) photographs of the corresponding gel swollen with 1,4-dioxane before and after freezing exhibiting distinct color changing (Reprinted with permission from Ref. [23]; Copyright (2015) WILEY-VCH); (c) Incorporation of DABBF into segmented polyurethane elastomers (Reprinted with permission from Ref. [24]; Copyright (2015) American Chemical Society); (d) Incorporation of DABBF into rigid silica networks (Reprinted with permission from Ref. [27]; Copyright (2016) American Chemical Society); (e) Schematic illustration of the synthesis of DABBF-modified CNCs (Reprinted with permission from Ref. [28]; Copyright (2017) The Royal Society of Chemistry)

In follow-up reports, they performed more detailed investigations with DABBF as the dynamic covalent mechanophore. Tensile deformation of the films of segmented polyurethanes, in which DABBF moieties were embedded in the soft segments, allowed for real-time and quantitative estimation of the stress (Fig. 5c)[24]. Following, they designed liner and four- and eight-armed star polymers with DABBF as mechanophore in the center. Samples with different molecular weights were synthesized and subjected to mechanical activation. Their studies showed that longer polymer chains induced mechanochemical transition more effectively and the star polymers had higher sensitivity to mechanical stress compared with a linear polymer in the bulk state[25]. They also found that the higher molecular mobility of the soft segment played an positive role in the repeated mechanochemical activation and autonomous regeneration of the mechanophore in thermoplastic elastomers. Such reversible mechanochromic dynamic covalent elastomers were expected to have applications when reversible detection of small mechanical forces and self-healing of potentially dangerous damage were desired[26]. Moreover, by functionalization of DABBF with alkoxysilane, polymer-inorganic composite materials with rigid networks crosslinked by DABBF were synthesized by means of a sol-gel method. According to EPR measurements, the mechano-responsive sensitivity of the composites was more than 50 times as high as that of DABBF monomers, which could be attributed to the suppressed recombination of the generated radicals by the rigid frameworks. This work thus provided a universal and versatile approach for designing highly mechano-responsive polymers by limiting their mobility (Fig. 5d)[27]. Most recently, Otsuka, Weder and their co-workers developed another polymer composite based on DABBF modified cellulose nanocrystals (CNCs). The limited molecular motions make DABBF highly sensitive to mechanical force and the mechanically actived radicals recombined slowly. Moreover, the DABBF modified CNCs could reinforce polymers and exhibt self-healable ability (Fig. 5e)[28].

The features of hexaarylbiimidazole (HABI) as color changing and radical mechanism under force were elucidated by Sijbesma and co-workers. As shown in Fig. 6, upon the force stimulus, HABI in polymeric architectures was broken into colored radicals and could futher initiate secondary radical polymerization of non-volatile acrylate through thiol species. Thus, the piece of work demonstrated clearly how we could alter destructive effect of mechanical force to perform constructive chemistry by choosing proper mechanophore which was able to combine optical reporting and reinforcement of polymers in a single molecular moiety[29].

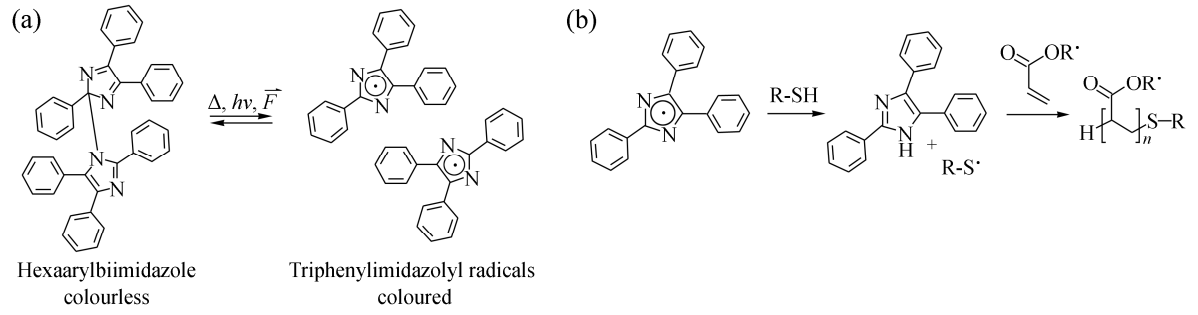


Fig. 6 (a) Reversible dissociation of HABI into TPI radicals; (b) Polymerization initiated by TPI radicals (Reprinted with permission from Ref. [29]; Copyright (2016) The Royal Society of Chemistry)

MECHANOLUMINESCENT POLYMERS

Compared to mechanochromism relying on UV-Vis spectral analysis, mechanically induced luminescence could significantly enhance sensitivity in the mapping of bond scission and stress evolution. Mechanoluminescent polymers include mechanofluorescent polymers and mechanochemiluminescent polymers, depending on whether any excitation light sources are required.

Chung *et al*. incorporated specific strained dimers of fluorophores, such as cinnamate[30] (Fig. 7a) and anthracene[31] (Fig. 7b), in polymer backbones. Upon cracking, the dimers cleaved into fluorescent monomers

and light emitted along propagating cracks of the polymer films. Similar strategy was employed by Craig and co-workers. They designed a coumarin dimer (CD) linked poly(methyl acrylate) (Fig. 7c). Activation of the mechanophore by ultrasound yielded coumarin chain-end functionalized polymers, which displayed the enhanced fluorescence. And the specificity for scission at the mechanophore was found to correlate with the distribution in the position of CD along the polymer main chain[32].

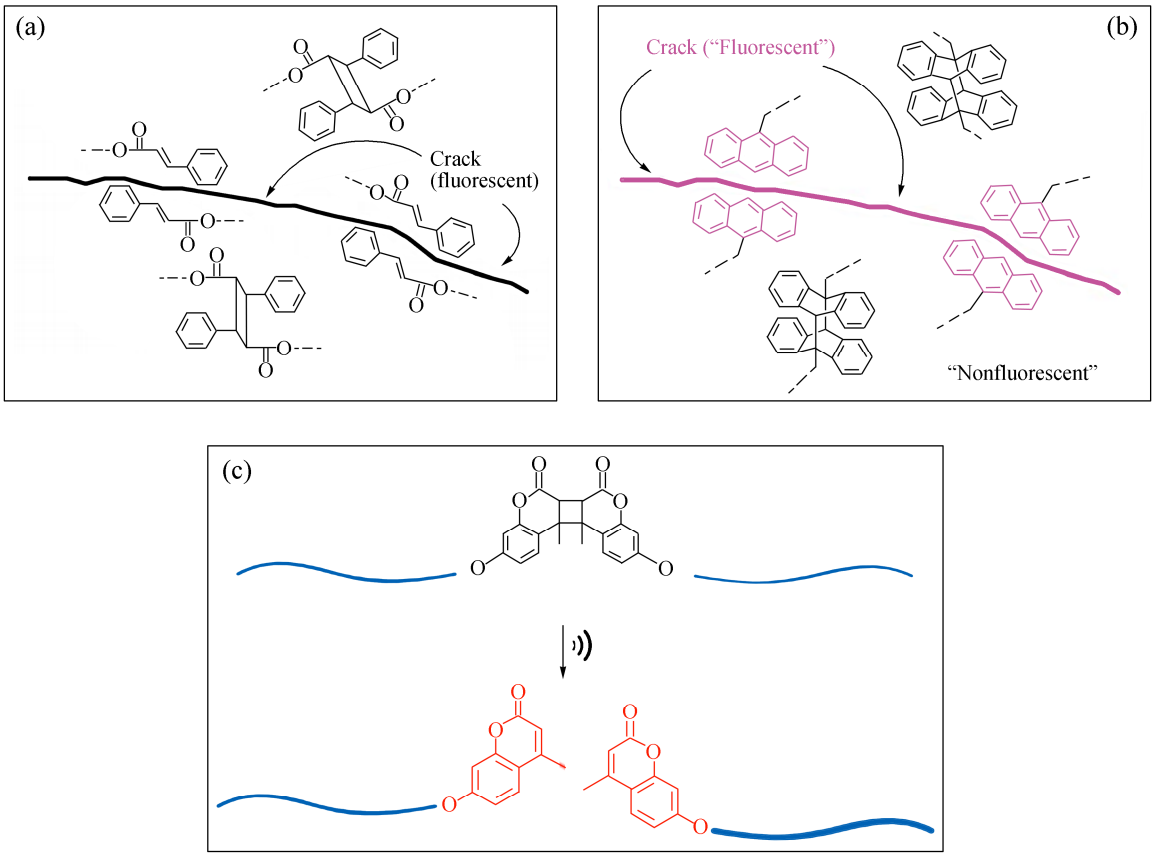


Fig. 7 Dimers of fluorophores: (a) cinnamate (Reprinted with permission from Ref. [30]; Copyright (2008) Elsevier), (b) anthracene (Reprinted with permission from Ref. [31]; Copyright (2012) The Royal Society of Chemistry) and (c) coumarin (Reprinted with permission from Ref. [32]; Copyright (2015) The Royal Society of Chemistry) as luminescent mechanophores

Cycloreversion reaction as a valid mechanochemical transition was revealed by Sijbesma and co-workers. They incorporated π-extended anthracene into polymeric Diels-Alder adducts. By mechanical activation, the polymers underwent cycloreversion reaction to release π-extended anthracene with intense fluorescence emitting (Fig. 8a). Compared to pristine anthracene, the π-extended anthracene has higher quantum yield, and thus afforded prospective stress probe with the improved resolution[33]. To illustrate the effect of self-assembly in mechanical activation, they developed micelles consisting of hydrophobic and hydrophilic diblock copolymer with off-center anthracene-maleimide Diels-Alder adduct as mechanophore in aqueous system (Fig. 8b). Triggered by ultrasound, the Diels-Alder adduct broke into polymeric fluorescent anthracene part and maleimide residue respectively, and the self-assembly of block copolymer was proved to promote the mechanochemical activity. Furthermore, the development of aqueous mechanofluorescent polymers is an important step to the application of force probes in true biological environments[34].

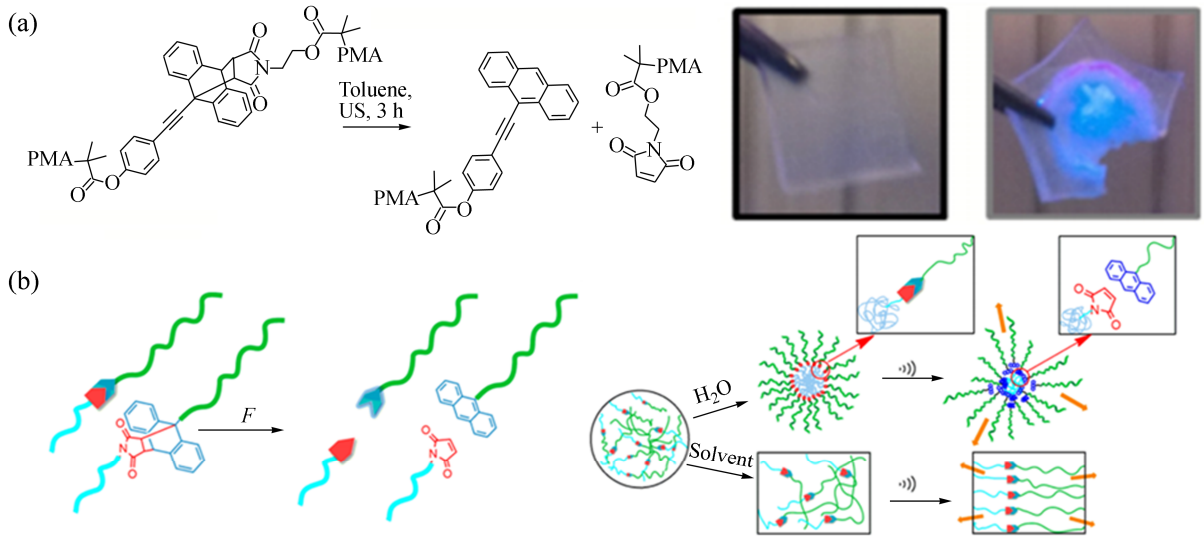


Fig. 8 Mechanically induced florescence associated with cycloreversion reactions: (a) π-extended anthracene and maleimide Diels-Alder adduct as the mechanophore, whose polymer film emitted intense blue fluorescence after compression (Reprinted with permission from Ref. [33]; Copyright (2016) The Royal Society of Chemistry); (b) Anthracene-maleimide adduct as the mechanophore when covalently attached in block copolymer micelles (Reprinted with permission from Ref. [34]; Copyright (2016) American Chemical Society)

Compared with mechanofluorescent polymers, mechanochemiluminescent polymers offered great increase of sensitivity in imaging of covalent bond scission since no additional excitation sources were needed. Up to now, although the chemiluminescent mechanophore is very limited, the progress of this field is exciting. The first mechanochemiluminescent polymer was prepared by Chen and Sijbesma *et al*. in 2012, using 1,2-dioxetane as the mechanophore. 1,2-Dioxetanes represent a class of high-energy molecules and are highly efficient chemiluminescent substrates with versatile applications in biological assays, sensors, *etc*[35]. They are thermally labile and generate two ketones on dissociation, one of which is in the excited state and emits a photon up relaxation. Among various 1,2-dioxetane derivatives, bis(adamantyl)-1,2-dioxetane, with energy barrier to the decomposition of 35 kcal·mol^{-1}, is thermally stable up to 190 °C, mainly because of the steric hindrance of the adamantyl substituents, but the ring can be opened at room temperature by mechanical force when covalently functionalized with polymer chains. Principle of the chemiluminescence from the polymers is based on the transduction of mechanical force along polymer chains to the strategically weakened O—O bonds, leading to the cleavage of the O—O bonds and concomitant blue light from the excited ketones (Fig. 9a)[36].

Bis(adamantyl)-1,2-dioxetane was designed as the center of linear acrylate polymers by living radical polymerization or as the cross-linker in polymer networks by photo-induced polymerization. Both the elastic polymer films could emit bright blue luminescence upon deformation within 20 ns of scission and with emission wavelength at 420 nm. This way, people were able to visualize failure of a polymer sample in tensile tests by looking at the position and intensity of its force-induced luminescence. The mechanical nature, rather than the thermal effect for the bond scission was confirmed by a series of control experiment. Later on, 1,2-dioxetane was found readily incorporated into the main chain of segmented thermoplastic elastomers (TPEs) under mild polycondensation conditions, such as polyurethanes, polyesters and polyamides (Fig. 9b)[37]. The 1,2-dioxetane thus could act as an autoluminescent probe for mechanistic studies of the TPEs failure, which involved covalent bond scission influenced by the molecular weight of the copolymers, strength of hydrogen bonding, amount of mechanophore, and strain rate. Further enhanced sensitivity and tuned emission color could be achieved by doping these polymeric matrices with different fluorescent acceptors (Fig. 9c). By means of energy transfer, they also estimated the singlet-triplet ratios and quantum yields, which were similar under mechanical activation as those under thermal activation[36].

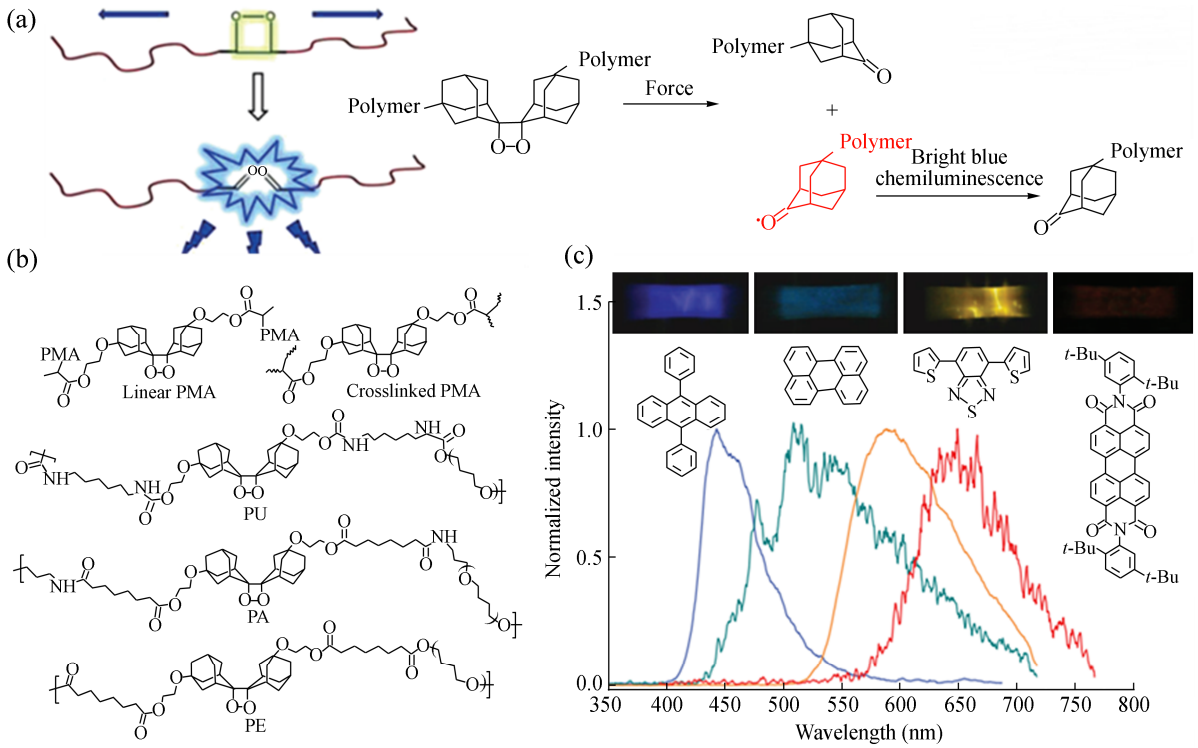


Fig. 9 (a) Schematic representation of mechanically induced chemiluminiscence from polymeric bis(adamantyl)-1,2-dioxetane (Reprinted with permission from Ref. [36]; Copyright (2012) Nature Publishing Group); (b) Structures of bis(adamantyl)-1,2-dioxetane linked linear PMA, crosslinked network and segmented copolymers (Reprinted with permission from Ref. [37]; Copyright (2014) American Chemical Society); (c) Fluorescence spectra of linear PMA films with different acceptors (Reprinted with permission from Ref. [36]; Copyright (2012) Nature Publishing Group)

Considering the transient and auto-luminescent nature of the light directly corresponding to the irreversible bond scission, the 1,2-dioxetane probe is particularly attractive for sensing damage and studying failure mechanisms of polymeric materials with unprecedented detail. An elegant example was reported by Creton and Sijbesma, in which the dioxetane mechanochemiluminescence was used to affirm a new toughening approach for elastomers. In this work, double-network principle once developed to make tough hydrogels was adapted to toughen up unfilled elastomers. The authors designed the elastomer with interpenetrating polyacrylate networks by sequential polymerization, stretched to different degrees by swelling the single and double network in the corresponding monomer sequentially. The highly stretched bond in the first network was sacrificed, thus broke firstly to dissipate energy and prevent crack propagation, as confirmed by incorporating the dioxetane chemiluminescent cross-linkers as sacrificial bonds as well. To this end, the crack luminescence map obtained from the mechanical hysteresis experiments clearly showed the bonds breaking distribution before crack tip and the dynamic shape of the damage zone (Fig. 10a)[38].

Mechanochemiluminescence also assisted in understanding the reinforced mechanism of metallosupramolecular gels developed by Craig *et al*. The pincer complexes were introduced into covalent networks of poly(4-vinylpyridine) (PVP) to create a family of hybrid polymer gels in which the covalent crosslinkers built up a permanent, stiff scaffold onto which reversible metal ligand coordinative crosslinkers were added. These reversible bonds in gels offered opportunities for preventing early bond scission events, because they allowed relaxation of stresses while maintaining many of the properties of their covalent polymer analogues. Such mechanism was consistent with the observations of substantial increase in strain at break and delayed onset of mechanoluminsece when 1,2-dioxetane was incorpated as a weak covalent crossilinker (Fig. 10b)[39].

Most recently, the 1,2-dioxetane mechanophore was utilized for studying the Mullins effect[40], in which the material appears to "remember" its previous maximum strain, of silica-filled poly(dimethylsiloxane) (PDMS) elastomer. Strain-induced light emission from 1,2-dioxetane cross-linkers in filled PDMS demonstrates that covalent bond scission contributes significantly to the irreversible stress-softening upon the initial extension (Fig. 10c)[41]. The 1,2-dioxetane was also used to investigate the covalent bond scission resulted from the sorption of chloroform by glassy poly(methyl methacrylate) (PMMA) networks. The physical mechanisms leading to solvent swelling-induced covalent bond breakage and macroscopic fracture could be systematically investigated with the mechanoluminescence probe (Fig. 10d)[42]. Altogether, mechanoluminescence offers an efficient approach with advantages of direct visualization, great temporal resolution, and molecular-level quantification to study localized fracture events in polymers.

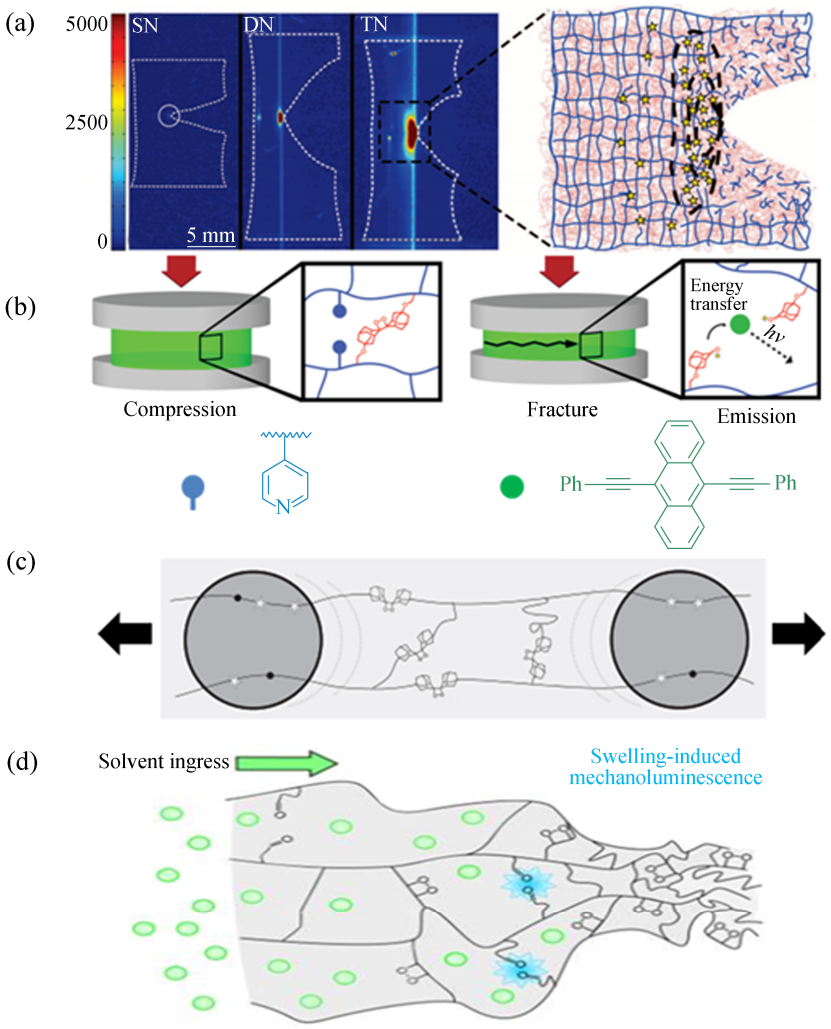


Fig. 10 (a) Mapping of where bonds break during crack propagation of single network (SN), double network (DN), and triple network (TN) samples and schematic representation of the sacrificial bond-breaking mechanism in front of the crack tip for the DN and TN (the first network is represented in blue, and the second and third net works are in red) (Reprinted with permission from Ref. [38]; Copyright (2014) American Association for the Advancement of Science); (b) Schematic representation of probing covalent failure of metallosupramolecular gels bearing dioxetane-functional crosslinks with mechanically generated chemiluminescence (Reprinted with permission from Ref. [39]; Copyright (2014) WILEY-VCH); (c) Simple schematic showing a proposed mechanism to account for the observed anisotropy in mechanoluminescence (Reprinted with permission from Ref. [41]; Copyright (2016) WILEY-VCH); (d) Schematic of swelling-induced mechanoluminescence (Reprinted with permission from Ref. [42]; Copyright (2017) American Chemical Society)

To activate the bond scission at lower force thresholds, cascade approach was applied into mechanoluminescent reaction. Sijbesma and co-workers explored the mechano-responsiveness of polytetrahydrofuran (pTHF) funcationalized palladium bis-*N*-heterocyclic carbene (bis-NHC) complexes which were borken to release *N*-heterocyclic carbene (NHC) with high basicity under sonication. They found the free NHC could deprotonate some specific chemiluminescent precursor, such as 3-(4-methoxyspiro[1,2-dioxetane-3,2′-tricyclo[3.3.1.13,7]decan]-4-yl)phenol (**1**) and ethyl(5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl)carbamate (**2**), to trigger the efficient chemiluminescence process (Fig. 11a)[43]. And the casade mechanoluminescence was also realized in solid state, with bis-NHC-Cu(I) as the mechanophore under pressure (Fig. 11b)[44]. With this cascade strategy, much higher quantum yield with lower force thresholds was achieved, leading to much greater sensitivity in probing bond scission processes.

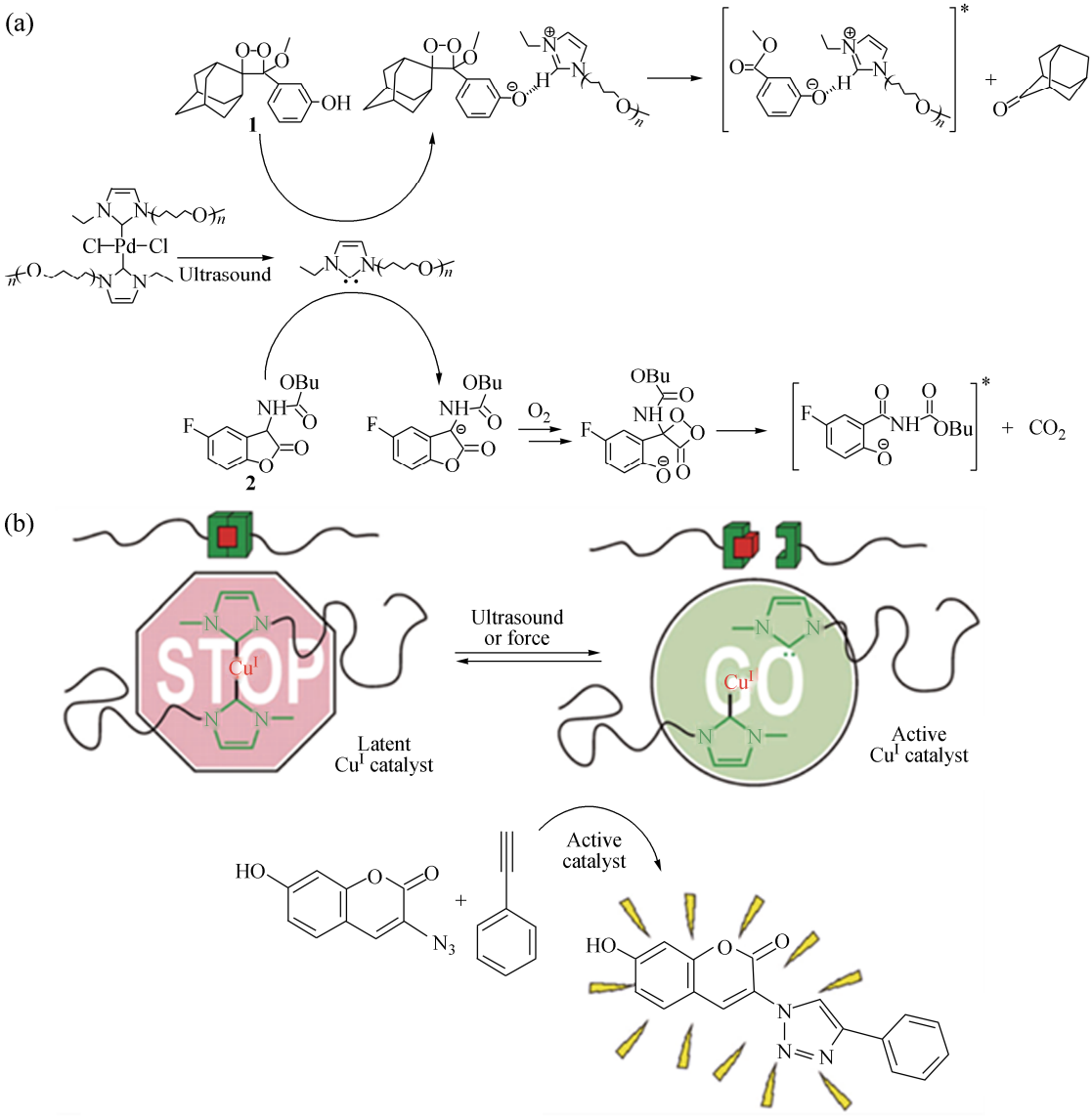


Fig. 11 Scission of NHC-metal coordination polymers (a) to initiate chemiluminescent decomposition with free carbine (Reprinted with permission from Ref. [43]; Copyright (2016) WILEY-VCH) and (b) to catalyze the fluorogenic click reaction (Reprinted with permission from Ref. [44]; Copyright (2015) WILEY-VCH)

CONCLUSIONS AND PERSPECTIVE

The use of polymer mechanochemistry to develop sensory materials was recognized early in the development of the field. Mechanochromic and mechanoluminescent polymers could visually report failure and damage on a submicrometer scale before macroscopic cracks became detectable. They represented an important category of mechano-responsive materials and allowed for sensing and comprehending the bond scission in polymers in more detail. The state of the art of the systems in which activation led to a facilely detectable spectroscopic change, *e.g.*, mechanochromism and mechanoluminescence, was introduced in this paper, which provided proofs of concept well. From a view of material applications, opportunities will arise including the following aspects:

(1) Although the sensory capabilities of the above mentioned mechanophores have been well recognized and characterized, their applicability for different polymeric materials and methods utilized to fabricate diverse bulk objects remain somewhat limited. Therefore, exploring new polymeric achitectures and technologies becomes vitally important for developing stress sensors and advanced tools of studying failure mechanism for versatile materials, such as thermoplastic elastomers (TPEs)[13, 23, 26, 37], tough hydrogels[38, 39], inorganic-organic hybrid materials[27, 28, 45], *etc*.

(2) Building up water-soluble and bio-compatible polymers to mimick mechano-transduction and bond scission in biological systems. We anticipate these research efforts can be a significant step toward the applications of force probes and drug-release in real biological environments.

REFERENCES

1 Zhurkov, S.N., Int. J. Fracture, 1984, 26: 295
2 Liu, K. and Piggott, M.R., Polym. Eng. Sci.,1998, 38: 60
3 Li, T.Q., Zhang, M.Q. and Zeng, H.M., J. Mater. Sci., 2000, 19: 837
4 Wisnom, M.R., Compos. Part A: Appl. Sci. Manufac., 2010, 41: 795
5 Caruso, M.M., Davis, D.A., Shen, Q., Odom, S.A., Sottos, N.R., White, S.R. and Moore, J.S., Chem. Rev., 2009, 109: 5755
6 Wiggins, K.M., Brantley, J.N. and Bielawski, C.W., Chem. Soc. Rev., 2013, 42: 7130
7 Black, A.L., Lenhardt, J.M. and Craig, S.L., J. Mater. Chem., 2011, 21: 1655
8 Yuan, W., Yuan Y. and Chen, Y., Acta Polymerica Sinica (in Chinese), 2016, (11): 1495
9 Yuan, Y., Yuan, W. and Chen, Y., Sci. China Mater., 2016, 59: 507
10 Pucci, A. and Ruggeri, G., J. Mater. Chem., 2011, 21: 8282
11 Davis, D.A., Hamilton, A., Yang, J., Cremar, L.D., van Gough, D., Potisek, S.L., Ong, M.T., Braun, P.V., Martinez, T.J., White, S.R., Moore, J.S. and Sottos, N.R., Nature, 2009, 459: 68
12 O'Bryan, G., Wong, B.M. and McElhanon, J.R., ACS Appl. Mater. Interfaces, 2010, 2: 1594
13 Lee, C.K., Davis, D.A., White, S.R., Moore, J.S., Sottos, N.R. and Braun, P.V., J. Am. Chem. Soc., 2010, 132: 16107
14 Jiang, S., Zhang, L., Xie, T., Lin, Y., Zhang, H., Xu, Y., Weng, W. and Dai, L., ACS Macro Lett., 2013, 2: 705
15 Wang, L.J., Zhou, X.J., Zhang, X.H. and Du, B.Y., Macromolecules, 2016, 49: 98
16 Fang, X., Zhang, H., Chen, Y., Lin, Y., Xu, Y. and Weng, W., Macromolecules, 2013, 46: 6566
17 Chen, Y., Zhang, H., Fang, X., Lin, Y., Xu, Y. and Weng, W., ACS Macro Lett., 2014, 3: 141
18 Chen, H., Yang, F., Chen, Q. and Zheng, J., Adv. Mater., 2017, 29, DOI: 10.1002/adma. 201606900
19 Robb, M.J., Kim, T.A., Halmes, A.J., White, S.R., Sottos, N.R. and Moore, J.S., J. Am. Chem. Soc., 2016, 138: 12328
20 Zhang, H., Gao, F., Cao, X., Li, Y., Xu, Y. and Weng, W., Boulatov, R., Angew. Chem. Int. Ed., 2016, 55: 3040
21 Wang, Z., Ma, Z., Wang, Y., Xu, Z., Luo, Y., Wei, Y. and Jia, X., Adv. Mater., 2015, 27: 6469
22 Wang, T., Zhang, N., Dai, J., Li, Z., Bai, W. and Bai, R., ACS Appl. Mater. Interfaces, 2017, 9: 11874
23 Imato, K., Irie, A., Kosuge, T., Ohishi, T., Nishihara, M., Takahara, A. and Otsuka, H., Angew. Chem. Int. Ed., 2015, 54: 6168

24 Imato, K., Kanehara, T., Ohishi, T., Nishihara, M., Yajima, H., Ito, M., Takahara, A. and Otsuka, H., ACS Macro Lett., 2015, 4: 1307
25 Oka, H., Imato, K., Sato, T., Ohishi, T., Goseki, R. and Otsuka, H., ACS Macro Lett., 2016, 5: 1124
26 Imato, K., Kanehara, T., Nojima, S., Ohishi, T., Higaki, Y., Takahara, A. and Otsuka, H., Chem. Commun., 2016, 52: 10482
27 Kosuge, T., Imato, K., Goseki, R. and Otsuka, H., Macromolecules, 2016, 49: 5903
28 Imato, K., Natterodt, J.C., Sapkota, J., Goseki, R., Weder, C., Takahara, A. and Otsuka, H., Polym. Chem., 2017, 8: 2115
29 Verstraeten, F., Gostl, R. and Sijbesma, R.P., Chem. Commun., 2016, 52: 8608
30 Cho, S.Y., Kim, J.G. and Chung, C.M., Sensor. Actuat. B-Chem., 2008, 134: 822
31 Song, Y.K., Lee, K.H., Hong, W.S., Cho, S.Y., Yu, H.C. and Chung, C.M., J. Mater. Chem., 2012, 22: 1380
32 Kean, Z.S., Gossweiler, G.R., Kouznetsova, T.B., Hewage, G.B. and Craig, S.L., Chem. Commun., 2015, 51: 9157
33 Göstl, R. and Sijbesma, R.P., Chem. Sci., 2016, 7: 370
34 Li, H., Göstl, R., Delgove, M., Sweeck, J., Zhang, Q., Sijbesma, R.P. and Heuts, J.P.A., ACS Macro Lett., 2016, 5: 995
35 Beck, S. and Koster, H., Anal. Chem., 1990, 62: 2258
36 Chen, Y., Spiering, A.J., Karthikeyan, S., Peters, G.W., Meijer, E.W. and Sijbesma, R.P., Nat. Chem., 2012, 4: 559
37 Chen, Y. and Sijbesma, R.P., Macromolecules, 2014, 47: 3797
38 Ducrot, E., Chen, Y., Bulters, M., Sijbesma, R.P. and Creton, C., Science, 2014, 344: 186
39 Kean, Z.S., Hawk, J.L., Lin, S., Zhao, X., Sijbesma, R.P. and Craig, S.L., Adv. Mater., 2014, 26: 6013
40 Schmoller, K.M. and Bausch, A.R., Nat. Mater., 2013, 12: 278
41 Clough, J.M., Creton, C., Craig, S.L. and Sijbesma, R.P., Adv. Funct. Mater., 2016, 26: 9063
42 Clough, J.M., van der Gucht, J. and Sijbesma, R.P., Macromolecules, 2017, 50: 2043
43 Clough, J.M., Balan, A., van Daal, T.L. and Sijbesma, R.P., Angew. Chem. Int. Ed., 2016, 55: 1445
44 Michael, P. and Binder, W.H., Angew. Chem. Int. Ed., 2015, 54: 13918
45 Li, J., Shiraki, T., Hu, B., Wright, R.A., Zhao, B. and Moore, J.S., J. Am. Chem. Soc., 2014, 136: 15925