# Dioxetanes as Mechanoluminescent Probes in Thermoplastic Elastomers

Yulan Chen and Rint P. Sijbesma*

Institute for Complex Molecular Systems, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Ⓢ *Supporting Information*

ABSTRACT: Mechanoluminescent 1,2-dioxetane units, which emit light upon scission of the strained 4-membered ring, were incorporated into the main chain of segmented copolymers with poly(tetramethylene oxide) soft segments and various hard segments. Test samples of the polymers emitted light upon applying strain. Polymers with hydrogen bonding urethane or amide groups in the hard segments showed stronger luminescence than polyester segmented copolymers of similar molecular weight. Increasing strain rate led to stronger luminescence. The positive effect of molecular weight on emission intensity in polyurethanes was interpreted in terms of decreased chain slippage when multiple hard segments anchor the polymer chain in different hard blocks. The results demonstrate that even chains with more than 50 hard segments slippage can be further reduced by increasing the degree of polymerization.
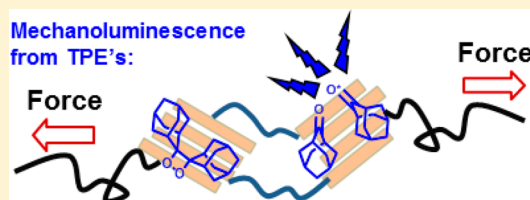
■ INTRODUCTION

In the past few years, mechanoresponsive polymers have attracted widespread attention.[1−4] This important research effort has been driven by the need for specific materials that can convert mechanical events into a measurable output, in self-sensing and self-healing materials, etc.[5−13] In most cases, such a response is based on noncovalent interactions.[9,10] Comparably few mechanoresponsive polymers are known to respond by changes in covalent bonding, which may limit the extent to which properties can be modified and the long-term stability in structural materials.

Recent progress in covalent polymer mechanochemistry has provided opportunities for the design of artificial stress-responsive materials.[14−22] A sensitive method that was recently introduced by us is based on mechanically induced chemiluminescence from a bis(adamantyl)-1,2-dioxetane unit that is incorporated in a polymer main chain or used as a cross-linker.[23] The strained 4-membered ring of 1,2-dioxetanes decomposes into two carbonyl moieties, one of which is in an electronically excited state.[24,25] Upon relaxation, blue light is emitted directly from the singlet excited state. Thermal dioxetane luminescence is extensively used in bioassays and diagnostics.[26,27] Our work successfully demonstrated that the dioxetane with the highest known thermal stability, bis-(adamantyl)-1,2-dioxetane, also gives rise to luminescence when decomposition is induced mechanically. Incorporating this specific unit into a polymethacrylate backbone, and mechanical activation of the polymer by deformation of a bulk sample at room temperature, led to dioxetane scission and concomitant light emission (Figure 1). Luminescent mechanophores are particularly attractive because the high intrinsic sensitivity of luminescence results in high spatial and temporal resolution of the signal and allows for probing of materials failure in unprecedented detail.

Thermoplastic elastomers (TPE's) represent an important class of engineering elastomers. Because of the unique combination of unusual features (including excellent mechanical strength, good tear and abrasion resistance, high elasticity, etc.) and the ability to be melt-processed, they have been applied in a very broad range of commercial and industrial fields.[28−30] However, applications of TPE's are limited by their susceptibility to degradation and failure. The most abundant class of TPE's are microphase-separated segmented copolymers which contain hard amide, urea, or urethane containing segments and soft amorphous segments. The hard domain structure and the boundary regions between the hard and soft segment have significant yet complex effects on fatigue failure process of polyurethanes. It is generally accepted that deformation mode consists of three stages: (1) the domain orientation stage, (2) the phase-mixing stage, (3) the segment orientation stage.[31] Generally, investigation of their failure mechanisms was performed with techniques such as ESR, IR, XRD, and NMR spectroscopy.[3,32,33] However, since these methods rely on mesoscopic characterization parameters, they are lacking sensitivity and resolution. More recently, much attention has been paid on exploiting and studying of optical responsive TPE's that change their color under mechanical force. Mechanochromic weak covalent bonds[29] and non-covalent bonds[34−36] in TPE's have been used to analyze molecular alignment or fracture in TPE's. Spiropyran (SP) containing polyurethanes were used as molecular level probes.[29] When the SP mechanophore was incorporated into either the soft or hard segment of segmented polyurethane, the
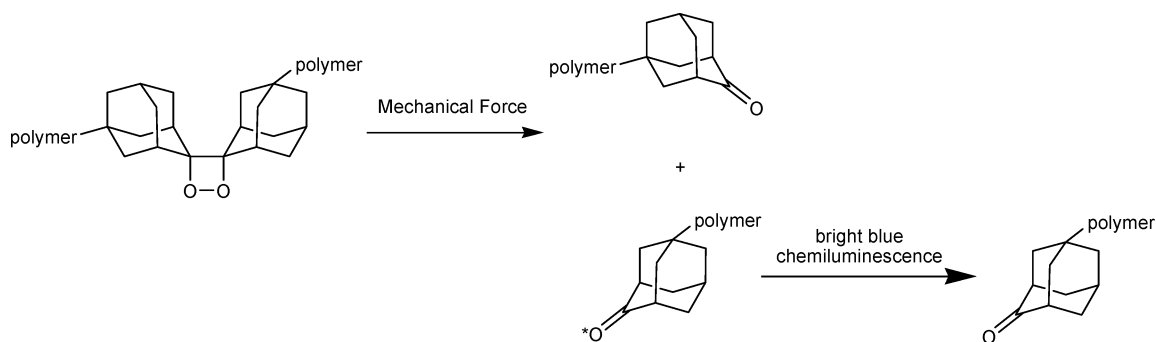
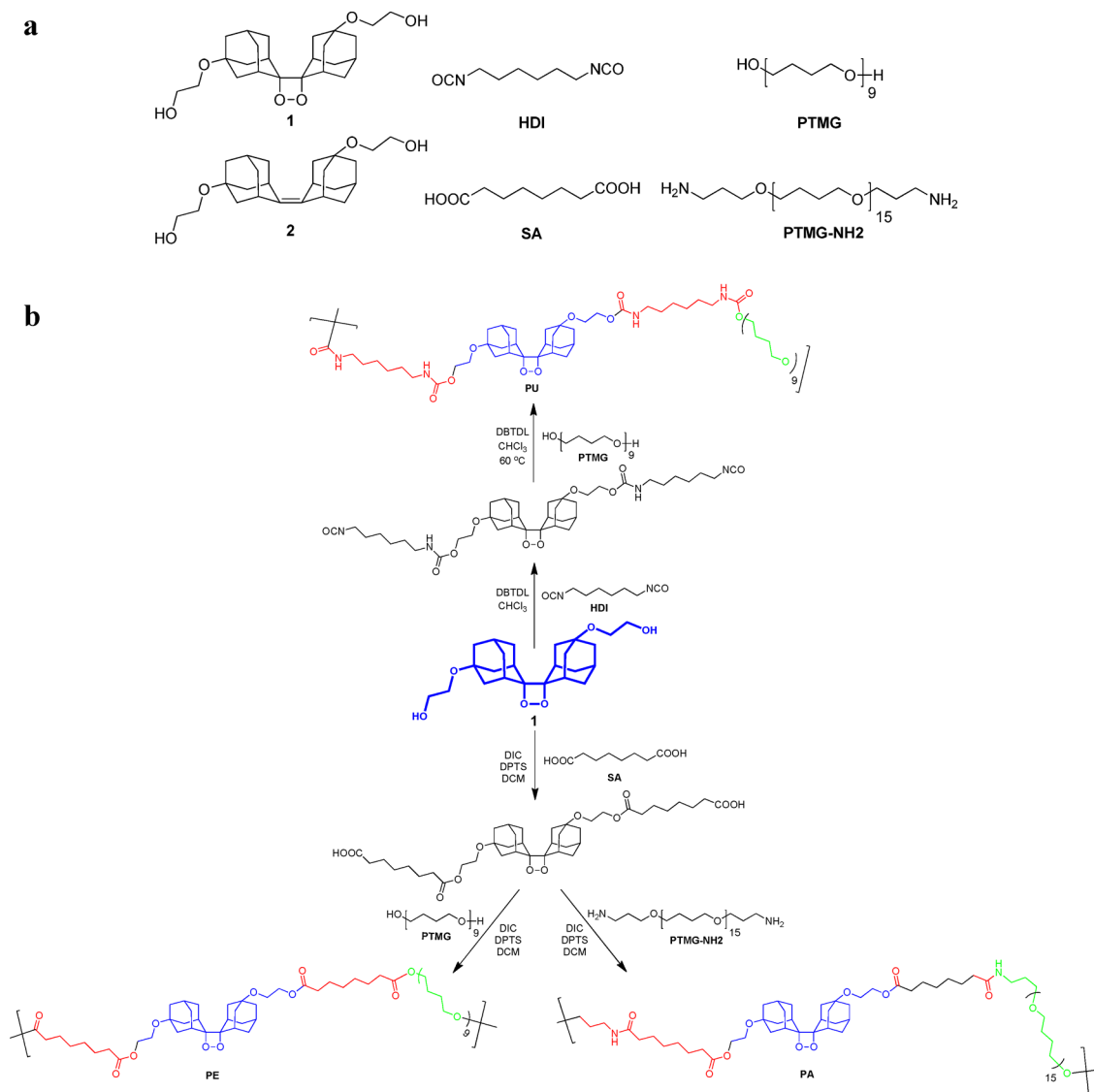**Figure 1.** Mechanically induced chemiluminescence from a polymeric bis(adamantyl)dioxetane.

Figure 2. (a) Structures of the components used to synthesize thermoplastic elastomers. (b) Synthetic scheme of TPE's and one possible sequence of blocks in the multiblock polymers.

strain and phase segregation of different domains could be tracked by monitoring strain-induced fluorescence changes.[37]

We reasoned that direct observation of chain scission events with high temporal and spatial resolution in TPE's would help gain understanding of their failure mechanisms. With this goal in mind, we decided to incorporate 1,2-dioxetane into thermoplastic elastomers. A class of 1,2-dioxetane-rich polyur-

ethanes (**PU**) was thus synthesized under mild conditions by a robust synthetic approach and subjected to mechanical deformation. By virtue of their excellent mechanical properties, such as toughness and high elasticity with low glass transition temperature, the segmented polymers synthesized by us exhibit pronounced light emission upon straining. By varying the extent of hydrogen bonding, dioxetane content, molecular

weight of the material, and the strain rate to which it was subjected, mechanoluminescent behavior was systematically investigated. To the best of our knowledge, this is the first example of a mechanoluminescent thermoplastic elastomer, and the work introduces an invaluable tool to study failure mechanisms of thermoplastic elastomers in unprecedented detail.

■ RESULTS

Synthesis and Characterization of TPE's. Segmented polymers containing a bis(adamantyl)dioxetane and different degrees of hydrogen bonding were designed and synthesized. Polyurethanes **PU-X**'s were obtained by combining 1,6-diisocyanatohexane (HDI), hydroxyl-terminated poly-(tetramethylene glycol) (PTMG, M_n = 650 g/mol), and hydroxyl bifunctionalized bis(adamantyl)-1,2-dioxetane (**1**).[23,38] Polyester thermoplastic elastomer **PE** was obtained using compound **1**, suberic acid (**SA**), and PTMG (M_n = 650 g/mol) as the building blocks, and polyamide **PA** was prepared from **1**, **SA**, and bis(3-aminopropyl)-terminated poly-(tetrahydrofuran) (PTMG-NH$_2$, M_n = 1100 g/mol). Finally, nonfunctional control **PU-r-X** was prepared by replacing one of the building blocks **1** to the bifunctional control **2** without dioxetane groups. The structures of these building blocks are shown in Figure 2a. An efficient two-step condensation method leads to the targeted segmented polyurethane **PU-1**, with the general structure depicted in Figure 2b. First, the bis-isocyanate-functionalized bis(adamantyl)-1,2-dioxetane was formed by reacting **1** with an excess of HDI in anhydrous chloroform, followed by polycondensation using bis-hydroxyl-functionalized PTMG as the chain extender, leading to multiblock polymers that contain soft (PTMG) and hard (HDI and **1**) segments coupled together by carbamate (urethane) linkages. Because the polymerization process involves different diols, the product is a complex mixture of macromolecules, each chain containing a statistical array of coupled segments.[28] Using a similar step growth polymerization approach through the bis-carboxyl-functionalized bis-(adamantyl)-1,2-dioxetane as an intermediate, **PE** and **PA** were successfully obtained under a diisopropylcarbodiimide (DIC)-mediated mild polyesterification or polyamidation procedure, respectively,[39,40] whose synthetic schemes and structures are illustrated in Figure 2b.

To reveal the effect of molecular weight and amount of dioxetane on the mechanoactivation process, a series of polyurethanes **PU-1**−**PU-4** with different molecular weights were synthesized by tuning the concentration of the reaction mixture and the polymerization time; **PU-r-5**−**PU-r-7** containing various proportions of bis(adamantyl)-1,2-dioxetane (by incorporating unfunctional control **2** as the repeating unit to keep the constant ratio of soft/hard segments) were prepared in a similar manner, as shown in Table 1. The chemical composition of each polyurethanes was determined by NMR and IR spectroscopy (Figure S3 in Supporting Information). The incorporation of bis(adamantyl)-1,2-dioxetane moieties and formation of urethane groups were estimated based on the peaks at 2.8 and 4.7 ppm in the ^{1}H NMR spectra, respectively. From **PU-r-5** to **PU-r-7**, the integration value of peak corresponding to the proton of bis(adamantyl) 1,2-dioxetane (δ = 2.8 ppm) increased proportionally, which is in line with the feed ratio of **2** and **1**. The infrared spectra of the **PU-X**'s showed characteristic peaks from urethane groups at 3320 cm^{-1} (hydrogen-bonded N−H stretch), 1720 cm^{-1} (free C=O

Table 1. Feed Ratios and Molecular Weights of PU-X's and PU-r-X's

	comp 1 (equiv)	comp 2 (equiv)	HDI (equiv)	PTMG (equiv)	M_n (kDa)
PU-1	1	0	11.05	10	43
PU-2	1	0	11.05	10	38
PU-3	1	0	11.05	10	12
PU-4	1	0	11.05	10	9
PU-r-5	0	1	11.05	10	48
PU-r-6	0.25	0.75	11.05	10	43
PU-r-7	0.5	0.5	11.05	10	42

stretch), 1683 cm^{-1} (hydrogen-bonded C=O stretch), and 1538 cm^{-1} (N−H in-plane bending). No peaks assigned to the starting NCO groups were observed. Bis(adamantyl)-1,2-dioxetane containing **PE** and **PA** were characterized by ^{1}H NMR and IR spectroscopy as well. For both polymers, the distinct proton peak at 2.8 ppm showed that the bis-(adamantyl)-1,2-dioxetane groups were integrated into the backbone. Peaks at 4.07 ppm from **PE** and 6.11 ppm from **PA** were ascribed to the protons from ester bonds (COO−CH_2) and amide bonds (CO−NH), respectively. The formation of ester and amide bonds was further confirmed from the characteristic IR peaks at 1733 cm^{-1} (C=O stretch) for **PE** and 3306 cm^{-1} (N−H stretch), 1635 cm^{-1} (C=O stretch), and 1543 cm^{-1} (N−H in plane bending) for **PA**. The number-average molecular weight (M_n) and polydispersity index (PDI) of the polymers were estimated based on GPC measurements using DMF as eluent and PEG as standards. DSC experiments performed on these as-synthesized semicrystalline polymers reveal the presence of a glass transition temperature (T_g) at about −60 °C and a melting point at about 45 °C from hard blocks for **PU** and **PA** as a elastic material and about 10 °C for **PE** as a gum-like material (Figure S4 in Supporting Information). The low glass transition temperature enables viscoelasticity of the materials at room temperature and facilitates mechanical force transduction along the polymer chains.

Mechanical Activation. The as-synthesized polymer samples **PU** are relatively tough elastomers at room temperature and easily processed at temperatures above 45 °C, indicating typical characteristics of thermoplastic elastomeric materials. When the bulk polymer sample was molded under mild compression at 45 °C for 2 min, a transparent and uniform film was formed after cooling. Sample bars for tensile deformation experiments were cut by blade to a rectangular shape (5 × 25 × 0.65 mm). Optomechanical tests were carried out on a rheometer equipped with two rotating drums, allowing for uniform extensional deformation. A camera was mounted in front of the rheometer to record videos in darkness. For instance, when the **PU-1** film was stretched at a rate of 10 s^{-1}, transient bright blue light emitted at the location of fracture indicated activation of the dioxetane group. The blue light can be easily recorded by a digital camera, even with the limited shooting rate of 30 frames/s (a representative picture of the whole setup is shown in Figure S5 of the Supporting Information).

To further confirm that this autoluminescence arose from mechanically induced dioxetane bond scission processes, instead of breakage of other chemical bonds or thermal processes, control component **2** or mechanophore small molecule was incorporated into **PU** via chemical (**PU-r-5**
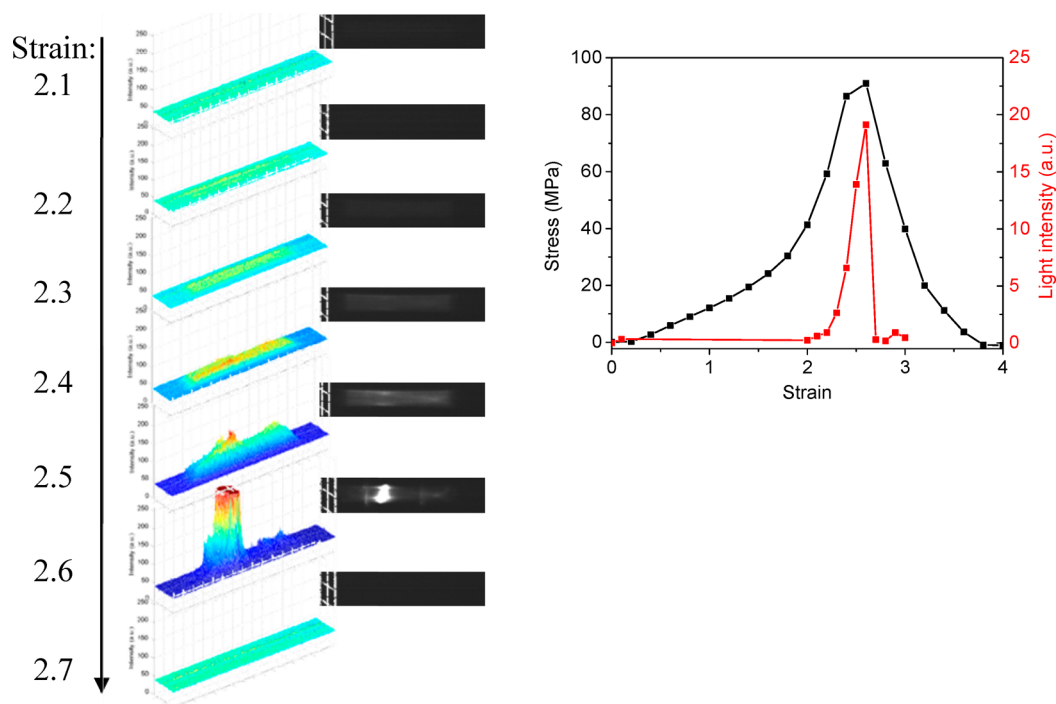
Figure 3. Stress and light intensity vs strain during stretching of a bulk film of **PU-1** containing 0.5 wt % 4,7-di(thiophen-2-yl)benzo$[c][1,2,5]$thiadiazole at strain rate of 20 s^{-1}. The left graphs correspond to optical images and intensity analysis of the sample during stretching. The analyzed intensity is based on the same region within the sample (one tick on the x- and y-axis corresponds to 2 mm). The level of the signal at strain <2.1 and >2.7 is nonzero because it derives from a noisy signal of individual camera pixels which is integrated over the whole film area.

without dioxetane) or physical (physically mixed film of plain **PU** and bis(adamantyl)-1,2-dioxetane) procedure, respectively.[41] When the control components are coupled into **PU**'s in such a way, no light was observed when bulk films from the two control systems were stretched and broken, indicating luminescence is only observed if mechanical force can be transferred to the dioxetane through a polymer chain. On the other hand, thermally induced light from **PU-1** can be observed at temperature above 150 °C. These results demonstrate the mechanical nature of the chemiluminescence from dioxetane containing **PU**'s. It is worth noting that under the same conditions the mechanoluminescence intensity from the **PU** elastomers is more than 6 times higher than that from the soft dioxetane containing poly(methacrylate) developed by us previously (Figure S6 in Supporting Information), which may indicate this dioxetane-containing **PU** would be more applicable as a self-sensing polymer on account of the higher sensitivity of its mechanoluminescent response.

Localization of Bond Scission in Space and Time. To learn more about their mechanoresponsive behaviors, the polymer films were subjected to mechanical testing. To facilitate the analysis and comparison, in all of the experiment illustrated below, 0.5 wt % 4,7-di(thiophen-2-yl)benzo$[c]$-$[1,2,5]$thiadiazole was incorporated into the polymer films as a singlet acceptor. This resulted in a color change of the emitted light from blue to yellow, with wavelengths (emission λ_{max} = 590 nm) where both human eyes and the camera are more sensitive. As a result of this, the total light intensity recorded through energy transfer to the acceptor was strongly enhanced. In a film of **PU-1** containing the thiadiazole dye, the recorded light intensity was at least 15 times higher than that in films of pure **PU-1**. Optomechanical tests were carried out

using the same rheometer described above, and light from the polymer film was recorded using a fast, sensitive scientific camera (pco.edge) as described in the Supporting Information; the transformation from mechanical force to light thus can be followed in detail. Representative images of the **PU-1** sample undergoing mechanical test are shown in Figure 3. The evolution of stress and light intensity vs strain during plastic deformation results in weak luminescence throughout the sample film at low stress, followed by a steep increase and concentration of light emission at the location of fracture immediately prior to failure. After the film was broken, no luminescence was observed. The fraction of light that originated from within 2 mm of the fracture region and in the 5 ms time span of the fracture frame relative to total light intensity is about 56% and 45%, respectively. It should be noted that due to the overexposure of the detector at the moment of fracture, these numbers are a lower limit, and more intense light emission may take place at fracture.

**Effect of Dioxetane Content on Light Intensity.** Compared to our previous study of mechanoluminescence in linear PMA, one of the advantages of the step-growth polymers is that the amount of dioxetane in each polymer chain can be varied easily, making this an ideal system to investigate failure mechanisms in elastomers. In order to develop a more quantitative understanding of mechanophore concentration on light intensity, **PU**'s with similar molecular weight (M_n of ca. 42 kDa) but different amounts of dioxetane were compared at a constant strain rate of 20 s^{-1}. For this study we compared **PU-1**, **PU-r-5**, **PU-r-6**, and **PU-r-7**, in which the relative ratio of dioxetane is decreased from 1, 0.5, 0.25 to 0 equiv (with respect to the ratio of unfunctionalized adamantylideneadamantane **2**), respectively. Figure 4 summarizes the accumulated light
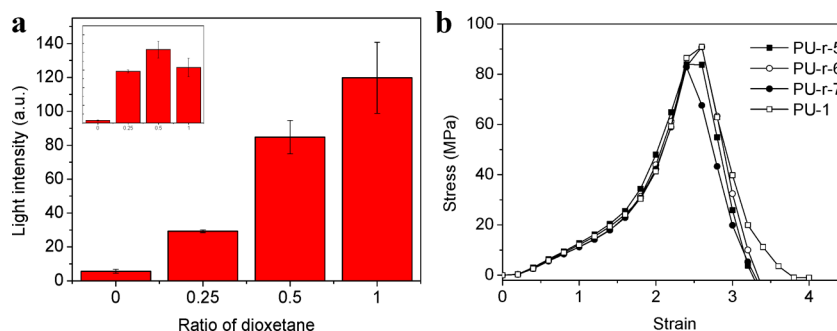
Figure 4. (a) Light intensity as a function of the ratio of dioxetane during stretching bulk films of **PU-1** and **PU-r-5**–**PU-r-7** containing 0.5 wt % 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole at a strain rate of 20 s^{-1}. Inset shows the light intensity divided by dioxetane content. Points represent average and standard deviation from 2 to 4 parallel experiments for each polymer. (b) The corresponding evolution of stress as a function of strain.
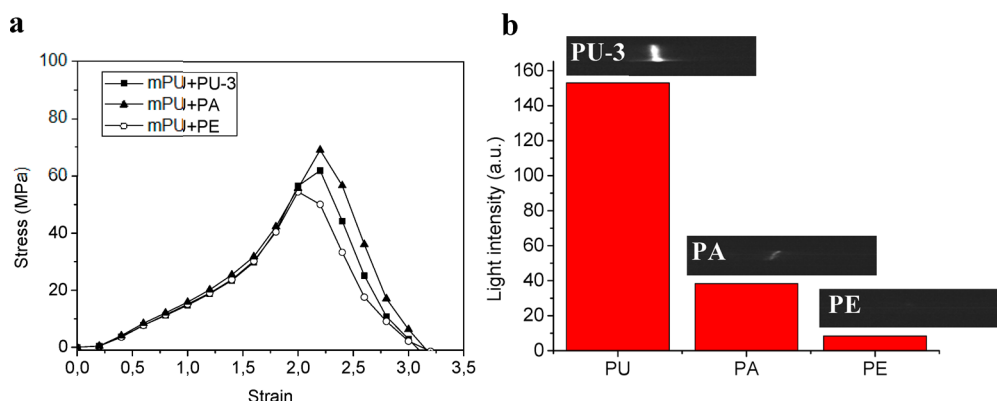
Figure 5. (a) Stress–strain curves of mixed films of plain **PU** and **PU-3**, **PA**, and **PE** containing 0.5 wt % 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole. (b) Optical images and the corresponding cumulative light intensity of **PU-3**, **PA**, and **PE** upon straining to failure.
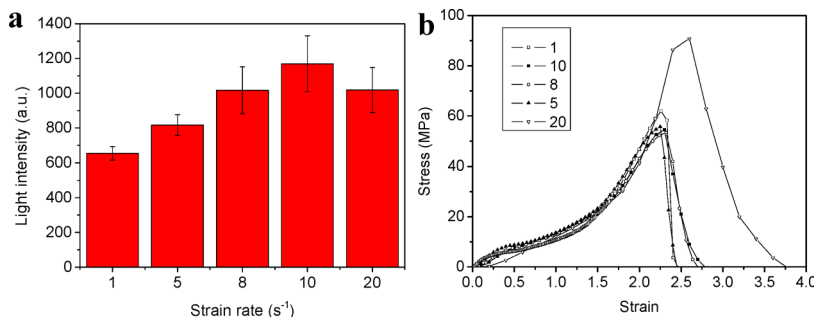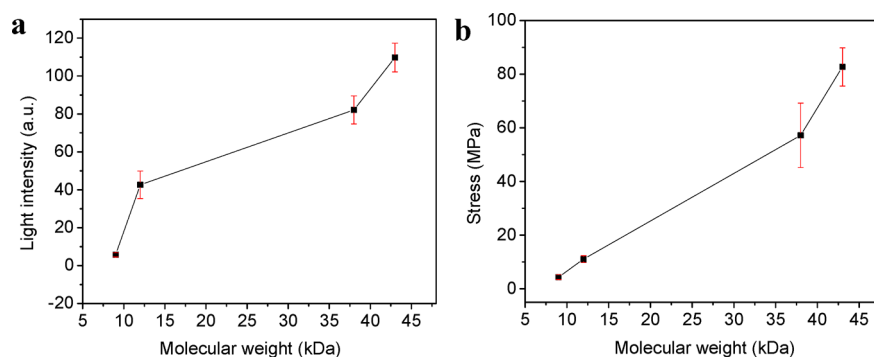

Figure 6. (a) Total light intensity emitted upon straining a film of **PU-1** containing 0.5 wt % 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole. Points represent average and standard deviation from 2 to 4 parallel experiments. (b) Stress–strain curves of **PU-1** at different strain rates.

intensity and mechanical property of the four polymers. Valuable information deduced from these data is as follows: (1) For the **PU**'s bearing up to 4.5 mol % of dioxetane groups, the covalently incorporated weak bonds do not significantly lower the mechanical strength of the bulk materials. (2) The total light intensity increases almost linearly with the increase of dioxetane fraction, meaning that corrected for the concentration of dioxetane (see inset Figure 4a), the intensity is almost independent of this concentration.

Effect of Hydrogen Bonding on Light Intensity. The effect of hydrogen bonding was studied further using dioxetane containing segmented polyurethane **PU-3**, polyamide **PA**, and polyester **PE**, with similar molecular weights of ca. 12 kDa, (33.3% w/w), incorporated in a matrix of polyurethane with a higher molecular weight (M_n = 42 kDa). The strain-induced activation of dioxetane units relies on the transfer of

macroscopic force to the individual mechanophores, embedded as physical cross-links in the TPE's. The force on the chains is determined on the rate of strain relative to the rate of disentanglement, which is determined by a number of factors, including chain length and number of hard segments, and by the interaction strength in the hard blocks. The strength of the interaction within hard blocks (consisting of aggregated segments) will therefore have a strong effect on the extent to which deformation leads to luminescence. Experiments were performed on three different mechanophore containing polymers to establish the role of hydrogen bonding on mechanoluminescence intensity. Because the polyester **PE** film is brittle, dioxetane containing segmented polyurethane **PU-3**, polyamide **PA**, and polyester **PE**, with similar molecular weights of ca. 12 kDa (33.3% w/w), were incorporated in a matrix of nonluminescent polyurethane with a higher molecular

Figure 7. Mechanoluminescent properties of **PU-1−PU-4** containing 0.5 wt % 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole at a strain rate of 20 s^{-1}. (a) Light intensity at break; (b) the corresponding stress at break as a function of molecular weight. Points represent average and standard deviation from 2 to 4 parallel experiments for each polymer.
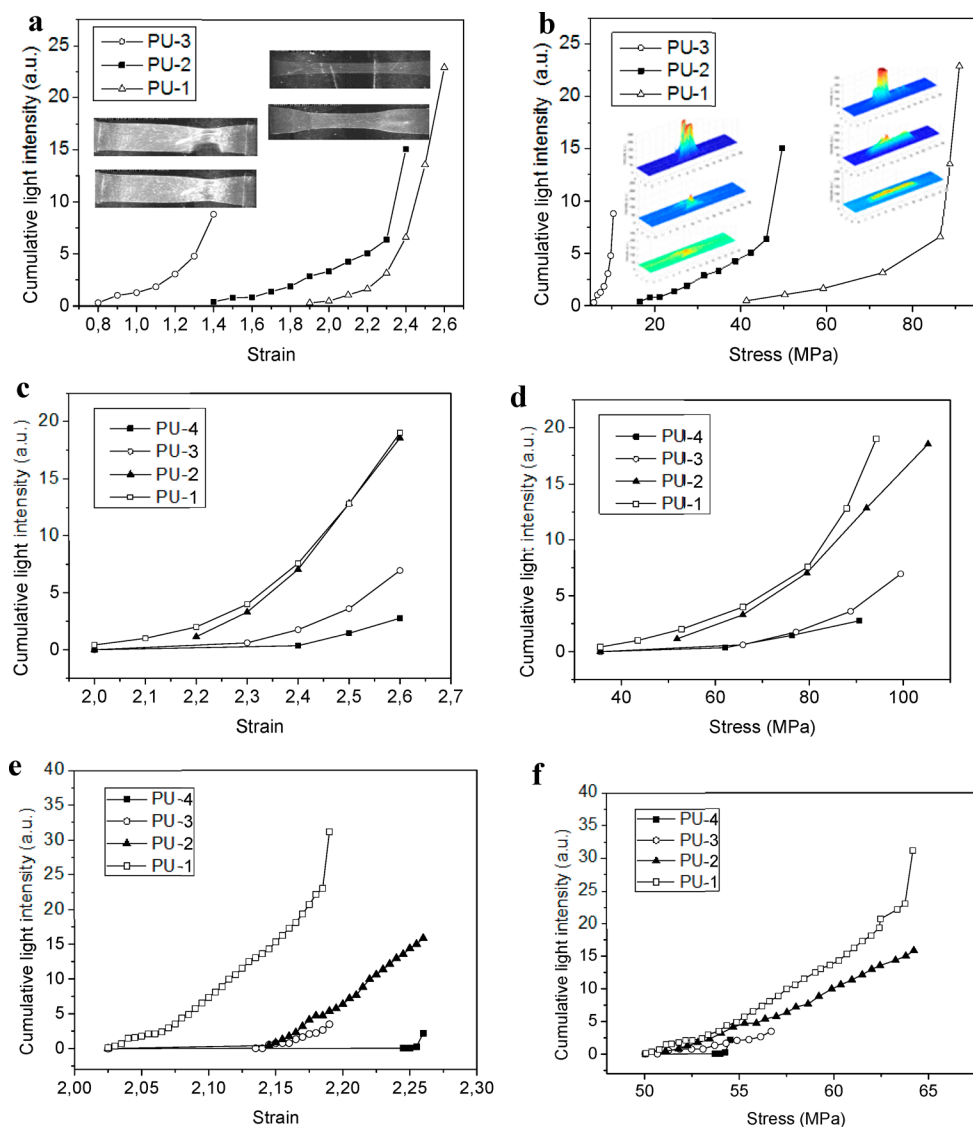
Figure 8. Cumulative light intensity vs strain (left) and vs stress (right) for **PU-1−PU-4** and their blends with 67 wt % of **PU-5**. (a, b) **PU-1−PU-3** at a strain rate of 20 s^{-1}. (c, d) Blends with **PU-5** at a strain rate of 20 s^{-1}. (e, f) Blends with **PU-5** at a strain rate of 1 s^{-1}. Insets show typical macroscopic deformation and intensity distribution of **PU-3** and **PU-1** during stretching.

weight (M_n = 42 kDa) to give elastic and uniform films. No macroscopic separation or aggregation was observed, and all three films could be subjected to controlled stretching. Stress−strain curves for the three films under stretching showed similar

mechanical properties (Figure 5a). Figure 5b displays typical images and the corresponding light intensity of the three polymer films that were strained at a rate of 20 s^{-1}. Interestingly, the light intensity is highly dependent on the

type of hydrogen bonding. For **PU-3**, the resulting dense hydrogen-bond network between the urethane groups allows most efficient transduction of mechanical force to dioxetane weak bonds and consequent most intense light among the three polymer films. **PA** with relatively low-density hydrogen-bond network emitted less light. In contrast, **PE** with chains that disentangle easier exhibits the lowest intensity of luminescence, indicating a lower bond scission probability.

Effect of Strain Rate on Light Intensity. To shed more light on the effect of strain rate on mechanoluminescence, **PU-1** films were subjected to failure at strain rate from 1 to 20 s^{-1}. As can be seen in Figure 6, stress increased at higher strain rate, and the total light intensity increased gradually with the increase of strain rate. At strain rate of 20 s^{-1}, the recorded light intensity decreased, which was most probably due to the saturation of camera detector and the time resolution of camera shutter. When it is assumed that the integrated light intensity is proportional to the number of broken dioxetane bonds, the continued increase of light intensity with strain rate leads us to believe that at lower strain rate only partial activation of dioxetanes in **PU** is achieved.

Effect of Molecular Weight on Light Intensity. Since the mechanical force accumulated along the polymer chain scales increases with molecular weight,[42] we conducted a series of experiments that probe the effect of molecular weight on the mechanoluminescent response of **PU**'s (from **PU-1** to **PU-4** with M_n varying from 9 to 43 kDa).

In the first set of experiments, **PU** films with acceptor were subjected to deformation at a strain rate of 20 s^{-1}. As expected, the mechanoluminescent effect observed in the different polymer films studied is directly related to the molecular weight of the polymers: the light intensity increases with increasing the molecular weight of **PU**'s, which is consistent with the changing of stress from the corresponding polymers, as shown in Figure 7a,b and Figure S7a in the Supporting Information. The absence of mechanically induced light from **PU-4** with molecular weight of 9 kDa, which was due to the weak mechanical strength of the film, suggested that there was a limiting molecular weight below which mechanochemical induced chain scission did not take place, while for **PU-1** with the highest molecular weight of 43 kDa, the detected light intensity increased significantly.

Real-time stress and light monitoring during the plastic deformation can communicate valuable information about material weaknesses and failure. The stress and strain at any given point were plotted with light intensity, assuming that the hightest stress is observed at the point of film fracture. As can been seen in Figure 8a,b, for each active film, the cumulative light intensity increased with stress and strain. Interestingly, the evolution of light intensity according to strain and stress is quite different from **PU-1** to **PU-3**: compared to the high molecular weight polymer film **PU-1**, lower molecular weight samples gave more light at lower stress. This marked discrepancy in mechanical activity can be rationalized in terms of different macroscopic deformation behaviors between these dioxetane containing **PU**'s: as shown by the insets in Figure 8, for lower molecular weight sample such as **PU-3**, deformation is initially highly localized, resulting in localized strain and stress to activate dioxetanes and relatively rapid occurrence of light emission, while for high molecular weight polymer, the deformation of films was more homogeneous so that both the stress and light distribution are more uniform.

In a second set of experiments, high molecular weight **PU-r-5** (67 wt %) without dioxetanes was used as a matrix, so that the mechanical properties of the obtained elastic films are approximately equal (Figure S7b,c in Supporting Information). In the mixed system, all of the films can be deformed uniformly and emit light, even for **PU-4** with molecular weight lower than the limiting value for emission in pure films. Local effects observed in the first set of experiments were excluded, and more information concerning the effect of polymer chain length was obtained. The evolution of stress and strain vs light intensity for each mixed films at strain rate of 20 s^{-1} and 1 s^{-1}, respectively, are summarized in Figure 8c–f. For all of the mixed **PU** films, uniform deformation before fracture resulted in continuous increase in light emission according to stress and strain. The cumulative light intensity at any given point was dependent on molecular weight of **PU**'s, which increased distinctly from **PU-4** to **PU-1**. The difference is more pronounced at lower strain rate.

■ DISCUSSION AND CONCLUSIONS

The current work shows that the bis(adamantyl)dioxetane is a sensitive molecular probe for investigating failure in TPE's. Failure of the material at the molecular scale can be directly read out as a transient and intense light signal. The observations from mechanical activation of these covalent polymers and their control analogues confirm the mechano-chemical nature of the dioxetane activation.

When increasing the amount of dioxetane in each **PU** backbone to as high as 4.5 mol %, the correlated light intensity did not change significantly. Since the fraction of dioxetanes broken after failure is very low,[43] the observation implies that dioxetanes are mechanically isolated and each dioxetane has the same probability of breaking, regardless of the number of dioxetanes in a chain. Moreover, our study showed that incorporation of mechanophores does not influence the macroscopic mechanical properties of the polymeric materials significantly. This is important, not only for further applications but also for a systematic comparison of dioxetane containing **PU-X**'s. It allows us to conclude that the amount of mechanophore activation is representative also for the amount of chain scission in unlabeled TPE.

The experiments show that upon straining chain scission in these TPE's takes place predominantly, but not exclusively, close to (within 2 mm) the line of macroscopic failure and also predominantly within 5 ms of macroscopic failure.

The strength of hydrogen bonding of the polymer chains to the matrix and the length of the chains both influence the amount of scission. However, even 12 kDa chains of PE, without strong hydrogen bonds to the matrix, were shown to break at a strain rate of 20 s^{-1}. Thus, although hydrogen bonding is effective in slowing down disentanglement, at high strain rates this interaction is not necessary for bond scission.

Based on results from all TPE's with different molecular weights, it is clear that stress is transferred to within the hard block so that in the mixed system of higher molecular weight matrix and a low molecular weight TPE containing dioxetane, transfer of macroscopic forces to dioxetane bonds can take place. Similar to most non-microphase-separated polymers, chain slippage is an effective mechanism for stress relaxation in TPE's. However, it is significant that even for the higher molecular weight TPE's, the amount of chain scission keeps on increasing with molecular weight. When going from **PU-2** (38 kDa) with approximately 50 hard segments per chain[44] to **PU-1**

(42 kDa), there is a significant increase in cumulative light intensity. This means that the effect on chain slippage of anchoring multiple hard segments in the hard blocks of the material has not saturated at 50 hard segments. Although somewhat suprising, this can be understood as the combined result of incomplete microphase separation (i.e., some hard segments are not anchored in the hard blocks) and the presence of a significant fraction of mechanically inactive physical cross-links (i.e., segments that form part of the same hard block).

The distinction with previous mechanochromic polymers as molecular level probes is that a transient and highly localized response is obtained. Mechanoluminescence from a range of TPE's indicates that the current design principles are general and readily applicable to other polymers.

In summary, the results presented here demonstrate that synthesis of TPE's with a tunable amount of dioxetane is straightforward. Upon straining to failure, these materials exihibit intense mechanoluminescence, which is influenced by the strength of hydrogen bonding of the polymer chain with the matrix, molecular weight of the polymer, amount of mechanophore, and strain rate. The effect of these parameters shows that the balance between strain rate and disentanglement rate determines the amount of bond scission. We furthermore conclude that disentanglement rates continue to decrease when chains are longer than approximately 50 hard segments. Mechanoluminescence from the multiblock polymers offers opportunities to obtain further insights into the failure mechanisms of thermoplastic elastomers and other polymers. The synthetic method, employing a mild and efficient polycondensation, is broadly applicable and can be scaled to large amounts of material. We therefore expect that this report will stimulate further work on the application of mechanoluminescence in step-growth polymers to study the detailed role of chain scission in their mechanical behavior.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details, characterization data, strain−stress data, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: r.p.sijbesma@tue.nl (R.P.S.).

Notes
The authors declare no competing financial interest.

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