Mechanochromic Polyolefin Elastomers

Cosimo Micheletti,[1] Luca Soldati,[1,2] Christoph Weder,[3,4] Andrea Pucci,[1]* Jess M. Clough[3,4]*

[1]Department of Chemistry and Industrial Chemistry and INSTM UdR of Pisa, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy

[2]Institute of Chemistry for Life and Health Sciences, École Nationale Supérieure de Chimie de Paris, PSL Research University, Centre National de la Recherche Scientifique, rue Pierre et Marie Curie 11, F-75005 Paris, France

[3]Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

[4]National Center of Competence in Research Bio-Inspired Materials, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

*Corresponding author e-mail: jessica.clough@unifr.ch, andrea.pucci@unipi.it

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Abstract

The optical detection of mechanical strain and stress in polymers is a powerful and convenient approach for studying deformation processes in these materials and identifying damage prior to failure in crucial components. We show here that mechanochromic behavior can be introduced via a straightforward one-step process that involves the modification of a commercial polyolefin elastomer (**POE**) grafted with reactive anhydride groups with small amounts (<0.8 wt%) of mechanochromic cross-linkers (**Loop** or **sPDI**). These motifs contain excimer-forming perylene diimides (PDIs) and react with **POE** to afford mechanochromic polyolefin elastomers (**POE-Loop** or **POE-sPDI**). The **Loop** motif contains two excimer-forming PDI moieties that can form folded structures in which the two PDIs *within* the **Loop** motif interact with each other, i.e. intra-**Loop**, while **sPDI** contains one PDI that can only form interactions with PDIs of other **sPDI** probes. Upon mechanical deformation of **POE-Loop** and **POE-sPDI**, the dye aggregates disassemble, and the ratio of monomer-to-excimer emission intensity increases. The data suggest that dye interactions *between* probes, i.e. inter-**Loop** or inter-**sPDI**, dominate the optical characteristics of both polymers.

Introduction

The mechanical characteristics of polymeric materials are critically important in many of their applications, which range from ballistic glass to scaffolds for tissue engineering. The desire to (better) monitor mechanical processes in these materials has driven the development of new experimental techniques that enable their mechanical deformation to be tracked via an optical readout. Mechanochromic polymers, which exhibit changes in their absorption or fluorescence properties in response to an applied strain or stress, have emerged as a powerful platform for both fundamental investigations[1,2] and damage-sensing in polymeric components.[3,4] One of the most commonly employed approaches to render polymers mechanochromic is to incorporate mechano-sensitive molecular motifs known as mechanophores,[3,5] which undergo mechanically induced transformations that give rise to a change in the motif's optical properties. In covalent mechanophores, activation involves the scission of covalent bonds and requires comparably large molecular forces (ca. 1 nN). Such processes are useful for monitoring permanent molecular damage. Another strategy to create mechanoresponsive probes is to exploit non-covalent, or supramolecular, interactions between optically active molecules that can form excimers,[6] charge-transfer complexes,[7,8] or are capable of energy transfer processes.[9] In contrast to many covalent mechanophores, the response of such supramolecular motifs can be reversible and is usually activated by smaller forces (ca. 10-100 pN).[10,11]

The incorporation of excimer-forming dyes into polymer matrices is a popular strategy to prepare materials in in which mechanochromic responses are produced by changes in supramolecular interactions.[12–15] This approach requires the dyes to form micro- or nanometer-sized aggregates, which are disrupted upon deformation so that the photoluminescence spectrum changes from excimer to monomer emission. Physical dispersions of excimer-forming probes can be particularly effective in semi-crystalline polymeric matrices, which support both the formation of small dye aggregates and their mechanical dissociation.[16] However, controlling the size of the dye aggregates, and thereby their mechanically induced dispersibility, can be quite challenging, especially in polymers that are amorphous or exhibit low crystallinity. Several strategies have been developed to overcome this problem in a range of semi-crystalline and amorphous polymeric matrices, including blending low-molecular-weight polymers functionalized at their termini with excimer-forming dyes (telechelic additives),[17,18] the covalent incorporation of fluorophores in the polymer backbone or as cross-linkers,[19–21] and the covalent incorporation of supramolecular mechanophores.[2,6,22] Telechelic additives are technically simple to incorporate, but the mechanochromic responsivity remains dependent on the solubility of the additive and host matrix.[12,17,23] Supramolecular mechanophores can impart mechanochromic behavior at relatively low concentrations and provide molecular-level information, but they require the *de novo* synthesis of mechanophore-functionalized polymers.[24,25] For technological applications, it would be attractive to develop a mechanochromic force-reporting platform that combines a range of desirable sensing characteristics. In particular, an unambiguous and preparation-independent spectral read-out and response across a wide strain range would be strongly advantageous. In addition, it should be possible to implement the platform in a range of commercial polymeric materials in a way that does not affect the mechanical properties of the host matrix, nor require complicated synthetic modifications.

Here we show that a loop-forming supramolecular mechanophore (**Loop**), which was recently reported by some of us,[2,6,22] can be readily introduced as a mechanochromic cross-linker into a technologically relevant polyolefin elastomer bearing reactive maleic anhydride groups (**POE-MAH**). The **Loop** mechanophore, prepared in three synthetic steps, contains two fluorescent perylene diimide (PDI) moieties that are connected by a short spacer (**Figure 1**). In the force-free state, the PDIs can form intra-**Loop** dimers that emit orange excimer fluorescence. When a force is applied to the mechanophore, the loops unfold and the PDIs are separated, leading to an increase in the intensity of green monomer emission. The degree of unfolding can be conveniently monitored with fluorescence spectroscopy or microscopy, using the ratio of the monomer to excimer emission intensities (I_M/I_E) as a metric. **Loop** mechanochromism was previously demonstrated in poly(methyl acrylate) and different polyurethanes, which incorporated the **Loop** mechanophore in their backbone.[2,6,22] Here, we incorporated the diol-functionalized **Loop** motif as a cross-linker into a commercial ethylene-1-octene copolymer grafted with reactive maleic anhydride groups (**POE-MAH**, *Figure* 1) using a straightforward reactive processing protocol. **POE-MAH** is a representative of an important class of materials that offer access to a wide range of thermal and mechanical properties[26,27] and find use in applications that range from thermoplastics[28] to compatibilizers for otherwise immiscible polymer blends.[29,30] We also prepared and investigated reference materials that were cross-linked with a corresponding motif that contains only as single PDI group (**sPDI**), in order to probe if mechanochromic responses can also be achieved by exploiting inter-**Loop** (rather than exclusively intra-**Loop**) interactions between the PDI dyes.

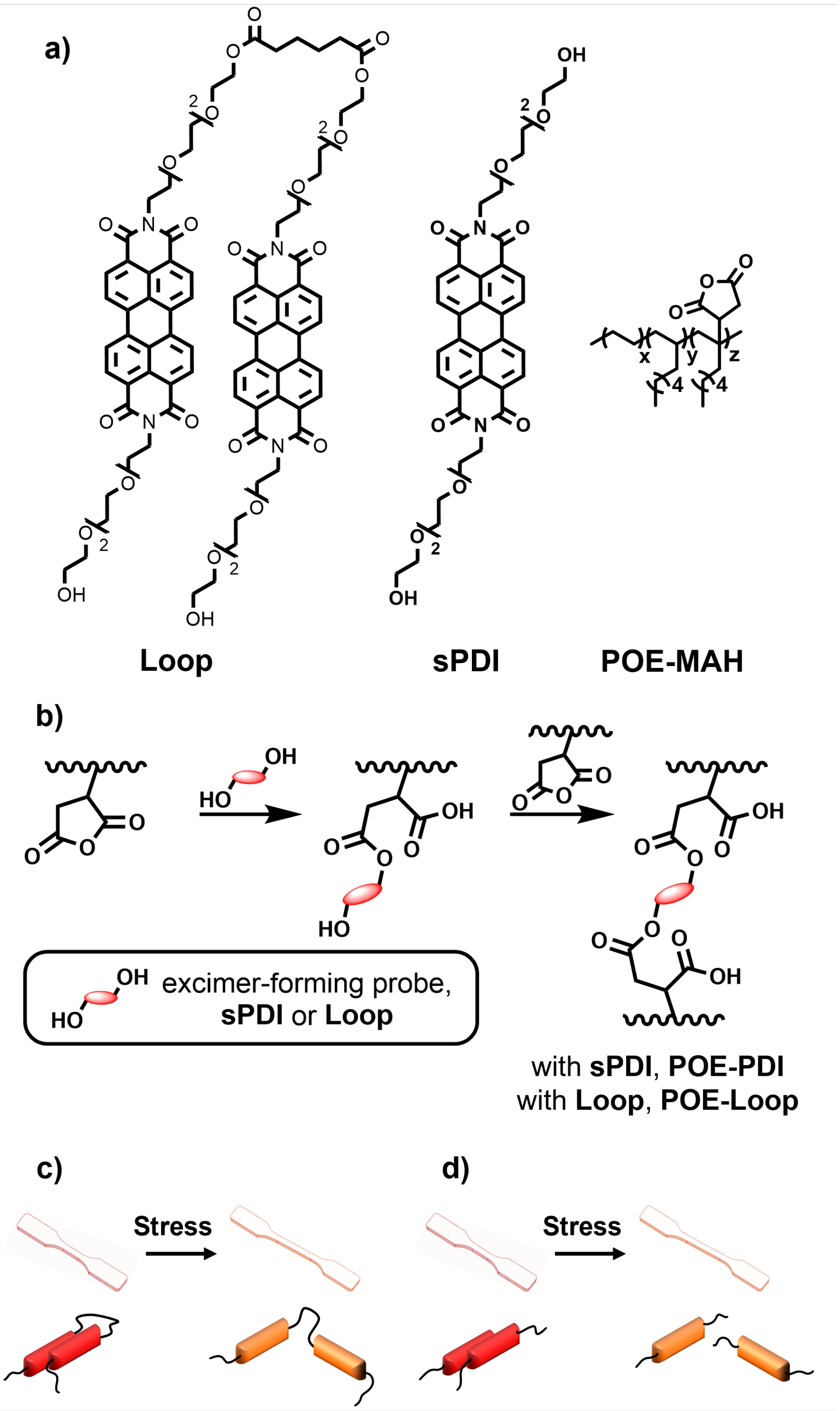

Figure 1. (a) Structures of **Loop** and **sPDI** probes, and the ethylene-1-octene copolymer grafted with 1 wt% of maleic anhydride, **POE-MAH**. (b) Schematic representation of the cross-linking reaction between the hydroxy groups of **Loop** and **sPDI** and the anhydride-grafted polymeric matrix under formation of **POE-Loop** and **POE-sPDI** respectively. Mechanochromic response based on the disruption of intra-**Loop** interactions for **Loop** (c) and of interactions between **sPDI** probes (d) respectively.

Results and Discussion

We decided to establish the functionalization methodology with the recently reported **Loop** mechanophore, which contains two perylene diimide (PDI) units connected by an aliphatic spacer (Figure 1). At zero force, attractive supramolecular interactions between the dye units lead to the formation of folded intra-**Loop** excimers. Mechanical deformation causes the loops to unfold, leading to an increase in the intensity of the monomer emission with respect to the intensity of the excimer emission. **Loop**-functionalized polymeric materials thus display a marked change in fluorescence color from orange (excimer) to green (monomer) as the materials are deformed mechanically. This mechanochromic response is visible by eye under UV light, and can also be characterized by spectroscopy or microscopy.[2,6,22] The **Loop** motif offers several attractive features as a mechano-sensing system, including sensitivity to a wide range of strains that spans elastic and plastic deformation, reversibility, thermal and chemical stability, relatively large spectral separation between the monomer and excimer peaks (ca. 100 nm), and relatively good quantum yields (0.22 for excimer, 0.72 for monomer).[31] Previously, some of us reported the incorporation of **Loop** in poly(methyl acrylate) and a range of polyurethanes by de novo synthesis.[6,22] For the purposes of this study, **Loop** bearing terminal hydroxy groups was synthesized (Figure 1a) following literature procedures.[22,31] We also prepared **sPDI**, consisting of a single PDI dye with the same functional handles as **Loop**, to explore the contribution of inter- vs. intra-**Loop** excimers to the mechanochromic response of the polymeric materials developed in the present study.

The assembly behavior of **sPDI** and **Loop** was first investigated in solution by means of UV-vis absorption and fluorescence spectroscopy. The UV-vis absorption spectra of chloroform solutions containing PDI concentrations of 4 μM show vibronic fine structures that are typical of PDI dyes, with an $A^{0\text{-}0}$ transition at 527 nm for both **sPDI** and **Loop**, and an $A^{0\text{-}1}$ transition at 490 and 492 nm for **sPDI** and **Loop** respectively (**Figure 2a**). The $A^{0\text{-}1}$ transition is more intense for **Loop** than for **sPDI**, indicating ground-state aggregation of the PDI dyes in **Loop** and the formation of the folded loop.[32,33] The $A^{0\text{-}0}/A^{0\text{-}1}$ ratio extracted from the spectra of **sPDI** (1.64) and **Loop** (1.06) are in agreement with values reported for dimeric and monomeric perylenes in DCM.[6,34] From this data, we estimate the fraction of folded dimers in **Loop** to be of the order of 80% in chloroform solution.[32,35,36] Moreover, excimer formation is indicated by the broad band at 624 nm in the fluorescence spectra of **sPDI** and **Loop** dissolved in chloroform (**Figure 2d** and **e**), and by the orange fluorescence color of the corresponding solutions (**Figure 2b** and **c**). **Loop** exhibits a much greater extent of excimer emission at the same molar concentration of perylene than **sPDI**, suggesting that the PDIs in **Loop** have an increased tendency to associate than in **sPDI**. We note that, in the fluorescence spectrum for **Loop**, the intensity of the excimer band remains relatively low compared to the monomer band because the fluorescence quantum yield of the excimer is lower than that of the monomer (0.22 for excimer, 0.72 for monomer), in spite of the high degree of folding expected on the basis of the absorbance spectra. In addition, the monomer bands in the fluorescence spectra of both **sPDI** and **Loop** exhibit a slight hypsochromic shift as the concentration of the probe molecule is decreased, which can be attributed to a decrease in internal absorption at lower concentrations.

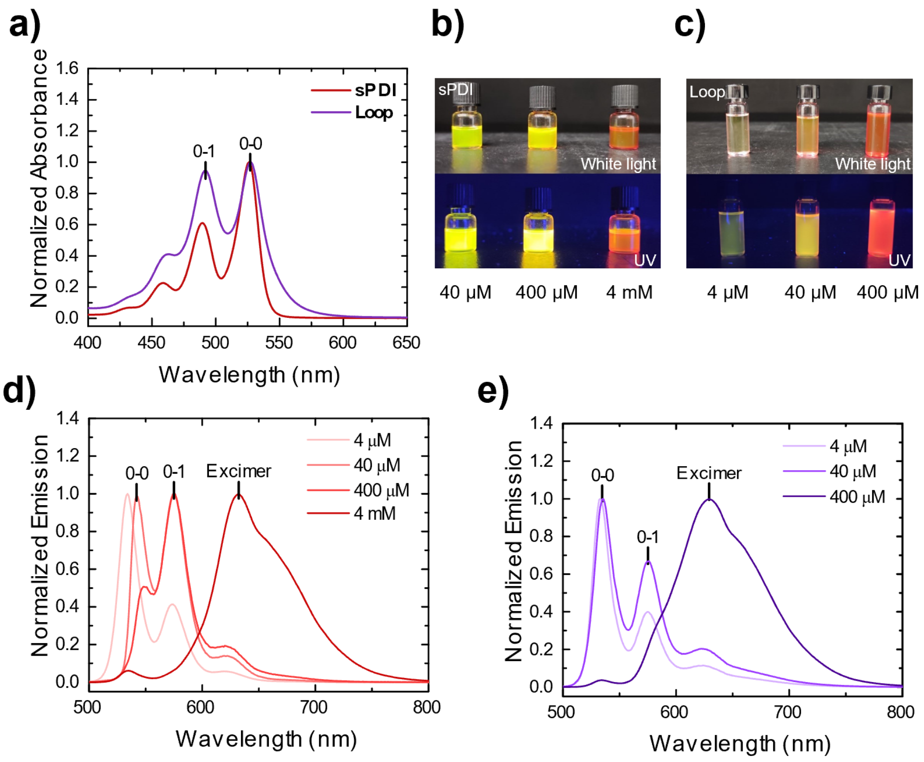

Figure 2. (a) Normalized UV-vis absorption spectra of **sPDI** and **Loop** in $CHCl_3$ at a PDI concentration of 4 µM. (b,c) Photos of solutions of (b) **sPDI** and (c) **Loop** in $CHCl_3$ under ambient illumination (top) and upon irradiation with a UV lamp (λ_{ex} = 365 nm) at different PDI concentrations. (d,e) Normalized emission spectra (λ_{ex} = 488 nm) of solutions of (d) **sPDI** and (e) **Loop** at different PDI concentrations in $CHCl_3$. Vibronic transitions are labelled for the monomer at **sPDI** and **Loop** concentrations of 40 µM.

With this understanding of the solution behavior of **Loop** and **sPDI**, we incorporated these motifs as excimer-forming cross-linkers into solid films of **POE-MAH** (Figure 1b). **POE-MAH** is an elastic ethylene-1-octene copolymer containing 1 wt% maleic anhydride grafts (**POE-MAH**), which can be cross-linked by reaction with diols. The equilibrium of the ester-forming reaction is strongly dependent on the temperature, and is shifted to the reactant (alcohol/anhydride) side of the equilibrium as the temperature is increased. Films containing 0.5, 0.05, 0.005 and 0.0005 equivalents of **Loop** or **sPDI** cross-linker with respect to the anhydride groups were prepared, and are referred to as **POE-X-0.5**, **POE-X-0.05**, **POE-X-0.005** and **POE-X-0.0005**, respectively, where "X" denotes **Loop** or **sPDI**. We note that the PDI concentration in **Loop**-containing samples is twice that in **sPDI**-containing samples, as each molecule of **Loop** contains two PDI units and **sPDI** only one. The films containing the highest concentration of excimer-forming cross-linker **POE-X-0.5** were found to contain microscopic aggregates of cross-linkers, and were therefore not studied in detail (Figure S1).[6] To ensure a uniform incorporation of the cross-linker, the films were first solvent cast from chloroform solutions containing **POE-MAH** (33 mg mL^{-1}), the corresponding cross-linker **sPDI** or **Loop**, and pTSA as a catalyst (5 mol% relative to MAH groups). After allowing the solvent to evaporate under ambient conditions, and subsequent drying at room temperature in vacuo, the solvent-cast films were compression molded (75 °C, 250 bar, 90 mins) to perform the cross-linking reaction, using adapted literature approaches.[37,38] The temperature was selected to maximize conversion of the anhydride groups to hemi-esters, while ensuring sufficient flow of **POE-MAH**.[37] After compression molding, the films were allowed to cool slowly in the press to room temperature, affording films with a uniform thickness (ca. 150 µm). Under ambient light, films of **POE-sPDI** and **POE-Loop** exhibit a reddish color, and under UV excitation (365 nm), they fluoresce orange at PDI concentrations above 0.005 eq (ca. 0.04 and 0.08 wt%, respectively) and yellow or green if the concentration of the excimer-forming probe was lower. The acid-catalyzed transformation of the anhydrides to hemi-esters was monitored by recording infrared (IR) spectra before and after compression molding (Figure

S2, Figure S3). The comparison of the spectra shows a shift in the C=O stretching that is indicative of the transformation of the dianhydride (1865 (w), 1788 (s) cm^{-1}) to the hemi-ester (ca. 1740 and 1711 – 1712 cm^{-1}, ester and carboxylic acid respectively) (Figure S3). Further evidence for cross-link formation was provided by swelling tests, which showed that the compression-molded film swelled, rather than dissolved, in a good solvent for **POE-MAH** (Figure S4). Moreover, liquid chromatography mass spectrometry (LC-MS) experiments confirmed that the ester groups in **Loop** did not decompose significantly in the presence of pTSA when refluxed in chloroform solution (Figure S5), suggesting that **Loop** is unlikely to decompose during compression molding.

With the **POE-sPDI** and **POE-Loop** films in hand, we investigated the effect of cross-linking on the thermal and mechanical properties of **POE-MAH**. The differential scanning calorimetry (DSC) traces of compression-molded **POE-MAH**, **POE-sPDI** and **POE-Loop** films exhibit a small endothermic peak at ca. 50 °C, indicating that all three matrices are largely amorphous and contain only a small fraction of crystalline domains that melt at this temperature (Figure S6). The thermal transitions of **POE-MAH** are not significantly affected by cross-linking with either **sPDI** or **Loop**. Furthermore, thermal gravimetric analysis (TGA) shows that the thermal stability of **POE-MAH** is retained after the cross-linking reaction (Figure S6) (thermal decomposition temperature 441-444 °C). The dynamic mechanical analysis (DMA) traces of **POE-MAH**, **POE-sPDI-0.005**, and **POE-Loop-0.005** are very similar (Figure S7, Table 1) and reveal comparable storage moduli and failure temperatures. This reflects that in **POE-sPDI-0.005** and **POE-Loop-0.005** the small fraction of cross-links does not affect the mechanical properties of the polymer, and stress transfer in these materials remains governed by entanglements and/or the physical cross-links imparted by the small fraction of crystalline domains. By contrast, the DMA traces of films containing the highest concentration of cross-linker, **POE-sPDI-0.5** and **POE-Loop-0.5**, show rubbery plateaus that extend to higher temperatures and the failure temperature is increased from ca. 150 °C (**POE-MAH**) to beyond 200 °C. Thus, when incorporated at higher concentration, the mechanophores form covalent cross-links that do change the thermomechanical properties of the materials in a perceivable manner.

Table 1. Dynamic mechanical analysis (DMA) results for **POE-X-0.005**, with data for **POE** and **POE-sPDI-0.5** shown for comparison.

	POE	**POE-sPDI-0.5**	**POE-sPDI-0.005**	**POE-Loop-0.005**
Storage Modulus (MPa) -80 °C	1649 ± 249	1799 ± 128	1279 ± 373	1966 ± 43
Storage Modulus (MPa) 25 °C	7 ± 3	8 ± 4	5 ± 4	8 ± 3
T_g (°C)	-30 ± 1	-31 ± 2	-28 ± 2	-30 ± 1
Failure Point (°C)	156 ± 9	196 ± 6	147 ± 5	161 ± 12
Failure Point (MPa)	0.03 ± 0.02	0.02 ± 0.01	0.01 ± 0.01	0.009 ± 0.005

Films of **POE-sPDI** and **POE-Loop** were characterized optically by UV-vis absorption and fluorescence spectroscopy. The UV-vis absorption spectra of **POE-X-0.05**, **POE-X-0.005** and **POE-X-0.0005** show A^{0-0} and A^{0-1} bands at ca. 550 and 490 nm respectively (Figure S8). Compared to the solution spectra, the bands are broader and red-shifted, and the intensity of A^{0-1} is significantly greater than that of A^{0-0}. The ratio of the absorption intensities of these two bands is ca. 0.5 for both **POE-sPDI** and **POE-Loop**, and does not appear to change significantly with the concentration of excimer-forming cross-linker in the investigated concentration range (0.05 – 0.0005 equivalents), which suggests significant ground state aggregation of the PDI dyes in these materials. By contrast, the fluorescence emission spectra depend strongly on the concentration of **Loop** or **sPDI**. The fluorescence spectra of **POE-sPDI-0.05** and **POE-Loop-0.05** exhibit only excimer emission at ca. 650 nm, while **POE-sPDI-0.0005** and **POE-Loop-0.0005**, containing the lowest concentration of cross-linker studied, exhibit primarily monomer emission, with bands at ca. 530 and 590 nm (**Figure 3**). At intermediate concentrations of cross-linker, the tendency of the PDI dyes in **POE-Loop-0.005** to associate is greater than those in **POE-sPDI-0.005**. The emission characteristics of the different materials are conveniently described by the ratio of the monomer to excimer emission intensities (I_M/I_E), which are reported for three independent samples of pristine film for several compositions of probe-functionalized POE in Table 2. Thus, the data reflect that while the **Loop** cross-linkers may form intra-**Loop** dye interactions, **sPDI** can also form excimeric aggregates in the POE matrix, which in turn suggests that also in the case of **Loop**, some inter-**Loop** interactions may be at play. Widefield fluorescence microscopy images acquired for films of POE-Loop or sPDI at 0.05 equivalents or below indicate no aggregation of the excimer-forming cross-linkers, suggesting that any PDI aggregates that formed are sub-microscopic in size (Figure S1).

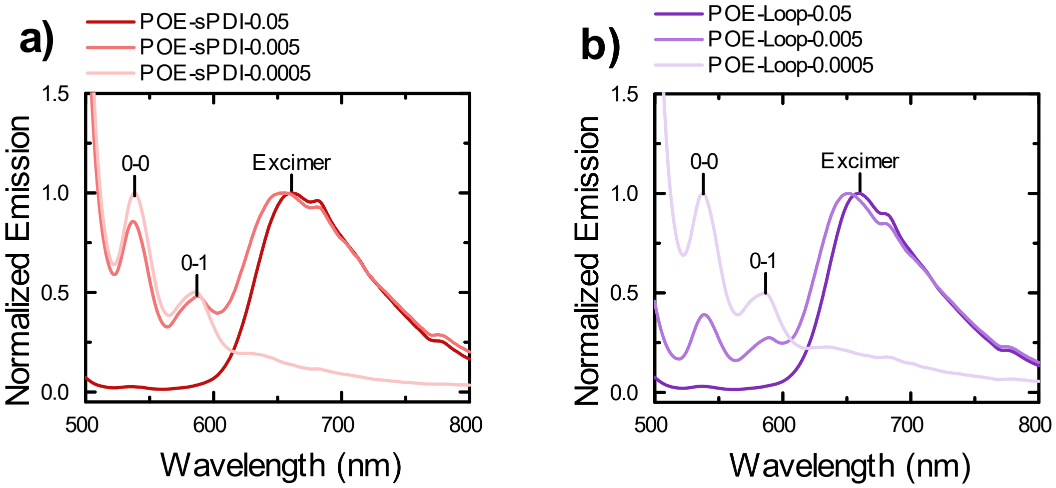

Figure 3. Normalized emission spectra (λ_{ex} = 460 nm) of **POE-sPDI** (a) and **POE-Loop** (b) containing different equivalents of excimer-forming cross-linker with respect to maleic anhydride grafts. Vibronic transitions are labelled for the materials **POE-X-0.0005**.

Table 2. I_M/I_E of pristine samples (at 0% strain) of **POE-sPDI** and **POE-Loop**, reported to two significant figures. Three films were measured for each composition. Errors indicate standard deviation from the average I_M/I_E for 3 separate samples.

	$(I_M/I_E)_{0\%}$			
	1	**2**	**3**	**Average**
POE-sPDI-0.05	0.027	0.025	0.032	0.028 ± 0.004
POE-sPDI-0.005	0.86	0.86	0.82	0.84 ± 0.02
POE-sPDI-0.0005	4.5	5.1	5.2	4.9 ± 0.4
POE-Loop-0.05	0.034	0.030	0.029	0.031 ± 0.002
POE-Loop-0.005	0.39	0.34	0.46	0.40 ± 0.06
POE-Loop-0.0005	4.4	4.4	4.1	4.3 ± 0.1

POE-X-0.05 and **POE-X-0.005** were selected for a detailed characterization of their optical responses in response to thermal and mechanical stimuli, on the basis that films with these compositions exhibit both excimer and monomer fluorescence emission peaks. Thermal tests on **POE-Loop-0.005** and **POE-sPDI-0.005** reveal that both materials show a strong thermochromic response (Figure 4, Figure S9). Films of these samples were heated from 25 to 175 °C, at a heating rate of 5 °C min^{-1}, while the changes in the fluorescence spectra were monitored in situ with an optical fiber, with spectra recorded every 2 seconds. For both **POE-Loop-0.005** and **POE-sPDI-0.005**, the intensity of the monomer band at 530 nm increases upon heating, as a result of thermally induced disaggregation of PDI dyes that are associated by either *inter*-probe interactions or *intra*-probe interactions for **Loop**. **POE-Loop-0.005** exhibits reduced sensitivity to temperature compared to **POE-sPDI-0.005**, which suggests that the nature of the interactions between the PDI motifs is different in the two materials, and possibly that **Loop** forms intra-**Loop** interactions, or inter-**Loop** interactions that are less labile than those of **sPDI**. The increase in I_M/I_E is non-linear with temperature, with a much greater increase observed above ca. 75 °C, indicating that this platform could be employed for mechanochromic sensing up to this temperature. We note that changes in temperature can also affect photophysical processes, which prevents the straightforward quantification of the extent of PDI association from the spectral changes. Nevertheless, the variation in I_M/I_E with temperature indicates that the extent of PDI association is not significantly affected by the chosen conditions of compression molding, which was conducted at 75 °C to ensure high conversion of the MAH groups. This could imply that at the processing temperature, some nano-sized aggregates of probe molecules are not dissociated and consequently do not react with the MAH groups of the polymeric matrix. The unreacted fraction of the probe molecules would be expected to show a weaker mechanochromic response, on the basis of control experiments with blended probe molecules (*vide infra*). However, we do not expect the presence of a small amount of unreacted probe molecules to significantly affect the mechanoresponse of **POE-Loop** and **POE-sPDI** significantly, which will likely remain dominated by the covalently coupled probe molecules for two reasons. Firstly, covalent coupling is expected to permit more efficient mechanotransduction of macroscopic forces to the probe molecules. Secondly, the fluorescence quantum yield of the monomer is approximately three times higher than that of the excimer, with the implication that the mechanoresponse is more sensitive to the unfolding or disaggregation of the coupled probe molecules.

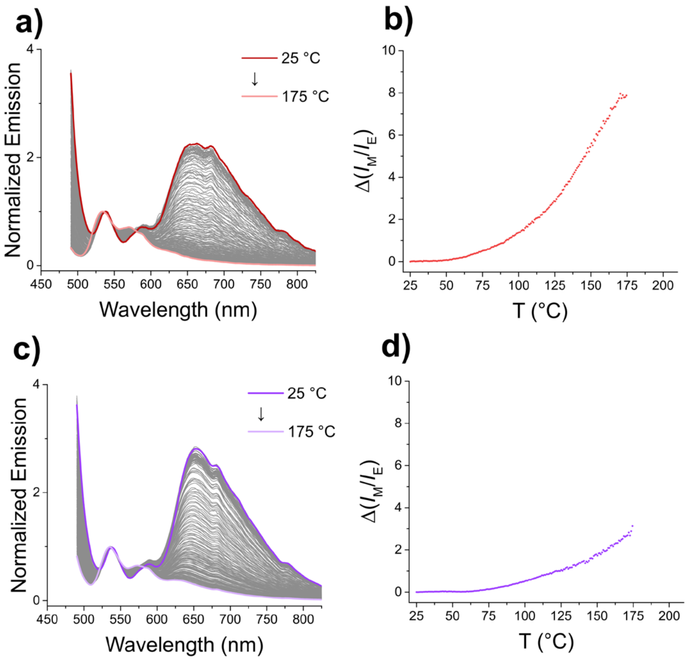

Figure 4. (a,b) Changes in fluorescence spectra of **POE-sPDI-0.005** upon heating (a) and corresponding changes in monomer-to-excimer emission intensity ratio with temperature (b). (c,d) Changes in fluorescence spectra of **POE-Loop-0.005** upon heating (c) and corresponding changes in monomer-to-excimer emission intensity ratio with temperature (d).

Having established the thermochromism of **POE-Loop** and **POE-sPDI**, we next investigated the mechanochromic behavior of these materials. For these experiments, the compression-molded films were cut into rectangular strips (thickness 150 µm x width 5 mm x length 20 mm) and subjected to uniaxial tensile deformation. When deformed uniaxially by hand and viewed under UV excitation (λ_{ex} = 365 nm), samples of **POE-sPDI** and **POE-Loop** both exhibit a red-to-yellow fluorescence color change that is clearly discernable by eye and indicative of the mechanically induced disassociation of PDI aggregates (**Figure 4**). To monitor mechanically induced I_M/I_E changes in situ during deformation, an optical fiber was positioned above the center of the samples that were subjected to uniaxial tensile strain in a microtensile testing device. Fluorescence spectra (λ_{ex} = 470 nm) were collected every second while samples were strained from 0 to 400 % at a strain rate of 50 % min^{-1}. The relationship between $\Delta I_M/I_E$ and strain is not significantly affected by the applied strain rate (Figure S10), as reported for **Loop**-containing PMA and PU.

To relate the optical changes to the applied strain, the metric $\Delta(I_M/I_E)$ was used, which refers to the difference in monomer-to-excimer emission intensity ratio at strain ε_1 $(I_M/I_E)_{\varepsilon 1}$ and at 0 strain (i.e., the pristine state), $(I_M/I_E)_0$, i.e. $\Delta(I_M/I_E)_{\varepsilon 1} = (I_M/I_E)_{\varepsilon 1} - (I_M/I_E)_0$. For both **POE-sPDI-0.005** and **POE-Loop-0.005**, $\Delta(I_M/I_E)$ increases linearly with applied strain (**Figure 5**, Figure S11). Similar values of $\Delta(I_M/I_E)$ over a strain range of 400% are obtained for both **POE-sPDI-0.005** and **POE-Loop-0.005** (Table 3). At other concentrations of cross-linker, $\Delta(I_M/I_E)$ also increases with strain, but the changes are significantly smaller (Table 3). In the case of **POE-X-0.05**, the spectra of the pristine films are strongly excimer-dominated, and upon deformation exhibit little change below ca. 50% applied strain, which could indicate the formation of larger PDI aggregates at higher cross-linker concentrations. The similarity in the mechanochromic responses of **POE-sPDI** and **POE-Loop**, in particular the way their responses are dependent upon PDI concentration, suggests that the disruption of inter-probe (inter-**sPDI** or inter-**Loop**) interactions drives the changes in optical properties in response to mechanical force. To explore the effect of covalent incorporation of the excimer-forming motif in POE, physical blends of **sPDI** and **POE-MAH** were prepared in the absence of pTSA catalyst and compression-molded at 75 °C for 5 minutes, rather than 90 minutes as for **POE-sPDI** and **POE-Loop**. The physical blends exhibit a considerably reduced mechanochromic response compared to **POE-sPDI**, for the same molar concentration of PDI (Figure S12). The fact that the physical blends still exhibit some mechanochromic behavior most likely indicates the presence of some larger-scale aggregates in the physical blends that are disaggregated by mechanical deformation of the polymeric matrix.[39] We also note that a small fraction of the probe molecules may also have reacted with the MAH groups of POE under the preparation conditions. Nevertheless, the covalent incorporation of the excimer-forming motifs seems to inhibit the formation of these larger aggregates that are more difficult to mechanically disperse, giving rise to an improved mechanochromic responsivity. Moreover, as observed in **Loop**-functionalized PMA and PU, the supramolecular nature of the mechanophore in **POE-Loop** enables these materials to detect mechanical events with relatively high strain sensitivity and over a wide strain range, compared to polymeric materials functionalized with “covalent mechanophores” whose activation requires covalent bond scission.

A further advantage of supramolecular mechanophores is that their activation is often reversible. We thus performed cyclic experiments to examine the elastomeric behavior of POE-MAH cross-linked with mechanochromic probes and to characterize the reversibility of the mechanochromic response. A sample of **POE-Loop-0.005** was deformed to a strain of 150% followed by immediate relaxation to 0% strain in five successive cycles, while its fluorescence spectrum was continuously monitored (Figure S13, Figure S14). The sample displayed some mechanical and optical hysteresis. Following relaxation to 0% strain after the first cycle, **POE-Loop-0.005** exhibited a slightly higher I_M/I_E than in its pristine state, indicating that some of the **Loop** motifs did not reaggregate upon relaxation (Figure S13, Table S1), and the deformation was not fully recoverable (Figure S14). Moreover, upon repeated deformation, I_M/I_E at 150% strain progressively decreased (Table S1), and the maximum stress reached also decreased with the number of cycles (Figure S14). Nevertheless, the mechanochromic response was reversible to a significant degree and correlated with the applied strain throughout the series of cycles, suggesting that the elastomeric behavior of the POE matrix was able to restore the initial optical properties of the material to a large extent. The elastic recovery and reversibility of the mechanochromic response could, in the future, be improved by tuning the cross-link density of the POE matrix.[40,41]

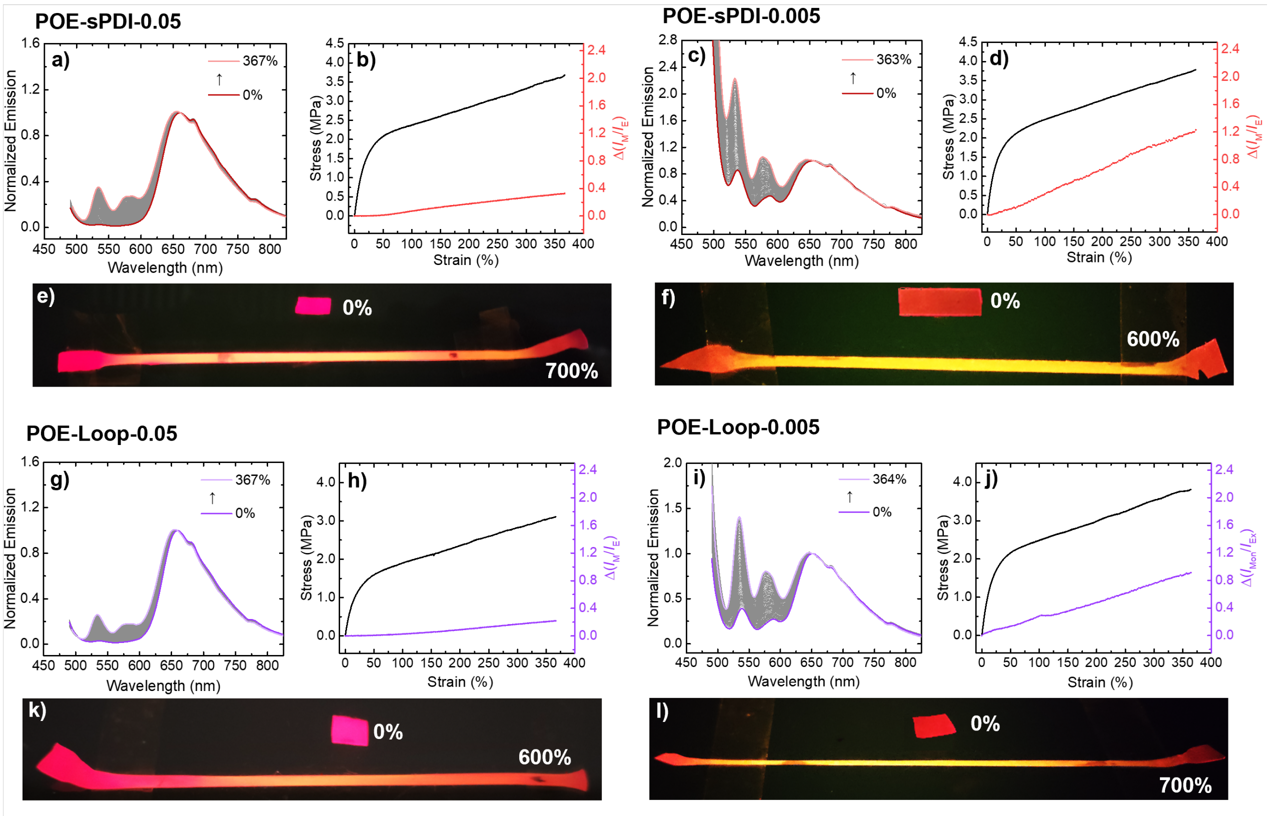

Figure 5. Emission spectra normalized by the peak intensity of the excimer band, recorded at different strains for **POE-sPDI-0.05** (a), **POE-sPDI-0.005** (c), **POE-Loop-0.05** (g) and **POE-Loop-0.005** (i), and corresponding stress-strain curves overlaid with $\Delta(I_M/I_E)$ vs. strain (right) for **POE-sPDI-0.05** (b), **POE-sPDI-0.005** (d), **POE-Loop-0.05** (h) and **POE-Loop-0.005** (j). λ_M and λ_E, corresponding to the wavelengths of the maxima of the monomer and excimer peaks respectively, were calculated from the spectra at strain 0%; values of I_M/I_E were calculated from the emission intensities at λ_M and λ_E. $\Delta(I_M/I_E)$ were obtained by subtracting the value of I_M/I_E at strain 0 from the value of I_M/I_E under applied strain, as described in the main text. All spectra are normalized to the excimer band and were acquired with λ_{ex} = 460 nm. Photographs of unstretched and stretched films of **POE-sPDI-0.05** (e), **POE-sPDI-0.005** (f) **POE-Loop-0.05** (k), and **POE-Loop-0.005** (l), all taken under Dark Reader 46B transilluminator equipped with a 450 nm LED source (Clare Chemical Research, U.S.A.).

Table 3. I_M/I_E at 0% and 350% strain, and absolute variation and relative variation (in brackets) between 0% and 350% for **POE-sPDI** and **POE-Loop** samples. Errors indicate standard deviation from the average I_M/I_E for 3 separate samples.

	$(I_M/I_E)_{0\%}$	$(I_M/I_E)_{350\%}$	$\Delta(I_M/I_E)_{350\%} = (I_M/I_E)_{350\%} - (I_M/I_E)_{0\%}$
POE-sPDI-0.05	0.028 ± 0.004	0.31 ± 0.03	0.282
POE-sPDI-0.005	0.84 ± 0.02	2.0 ± 0.2	1.16
POE-sPDI-0.0005	4.9 ± 0.4	5.4 ± 0.2	0.5
POE-Loop-0.05	0.031 ± 0.002	0.21 ± 0.02	0.179
POE-Loop-0.005	0.40 ± 0.06	1.3 ± 0.1	0.9
POE-Loop-0.0005	4.3 ± 0.1	5.0 ± 0.3	0.7

Conclusions

In summary, we demonstrated that the previously reported **Loop** mechanophore containing two PDI dyes can be incorporated as a cross-linker directly in commercially relevant polyolefin elastomers without their synthetic modification. We achieved this with a facile, one-step methodology based on compression molding, which is a widely used technique in polymer processing. This approach imparted mechanochromic behavior to polymeric matrices at low incorporation contents of excimer-forming probe, compared to existing strategies. Complementary studies on materials containing the single PDI **sPDI** cross-linker suggest that inter- rather than intra-**Loop** interactions dominate the mechanochromic response of both **Loop** and **sPDI**-functionalized materials. This result suggests that the polymeric matrix plays an important role in facilitating the successful self-assembly of supramolecular mechanophores. We expect that the preparation methodology presented here can be applied to many other kinds of mechanophores, supramolecular and covalent, to render a wide variety of polymers mechanochromic. In addition to maleic anhydride-functionalized thermoplastics and rubbers, the methodology presented here could be extended to other cross-linked polymeric materials, such as cross-linkable thermoplastics and melt-processable thermosets, or vitrimers, based on thermally activatable cross-links, by modifying the reactive groups of the mechanochromic cross-linker. Moreover, the study has implications for the design of supramolecular mechanochromic polymers, suggesting, for example, that polymeric architectures with pendant probe molecules may also enable optical sensing of mechanical deformation with high sensitivity. Given that the preparation of **Loop** requires four synthetic steps and column purification, a simpler pendant-based design may be particularly impactful in reducing the synthetic barrier to the implementation of mechanochromic cross-linkers in polymeric matrices.

Data availability

The source data of this study are available from the Zenodo repository at DOI: XXX.

Conflicts of interest

There are no conflicts to declare.

Supporting Information

Supporting Information PDF contains supporting Figures S1-14 and Table S1, and a detailed description of materials and methods.

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