

Supporting Information

Mechanochromic Polyolefin Elastomers

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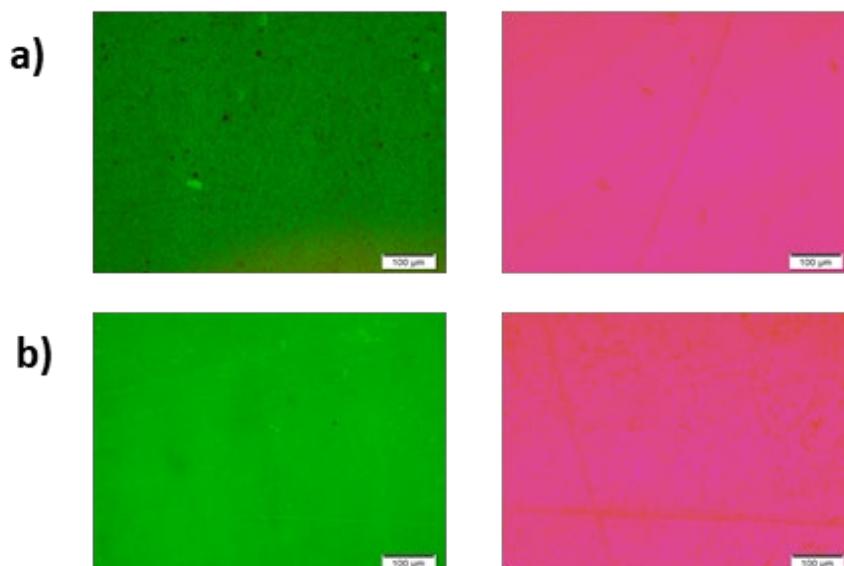


Figure S1. Epifluorescence microscopy of **POE-sPDI-0.5** (a) and **POE-sPDI-0.05** (b), taken with a blue excitation/green emission filter (λ_{ex} : 480/40 nm; λ_{em} : 535/50 nm left column), and a blue excitation/red emission filter (λ_{ex} : 469/35 nm; λ_{em} : 620/52 nm, right column). The aggregates in **POE-sPDI-0.5** appear as dark spots in the image taken through the green filter in (a).

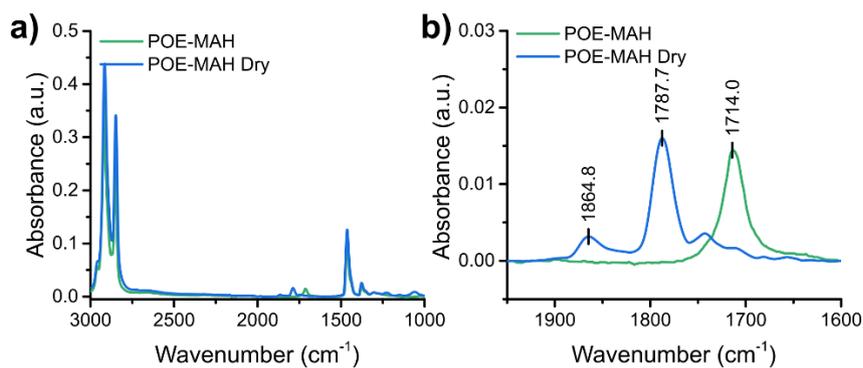


Figure S2. FT-IR (ATR mode) spectra of (a) **POE-MAH** before and dried after thermal treatment, with (b) zoom-in of carbonyl stretching region.

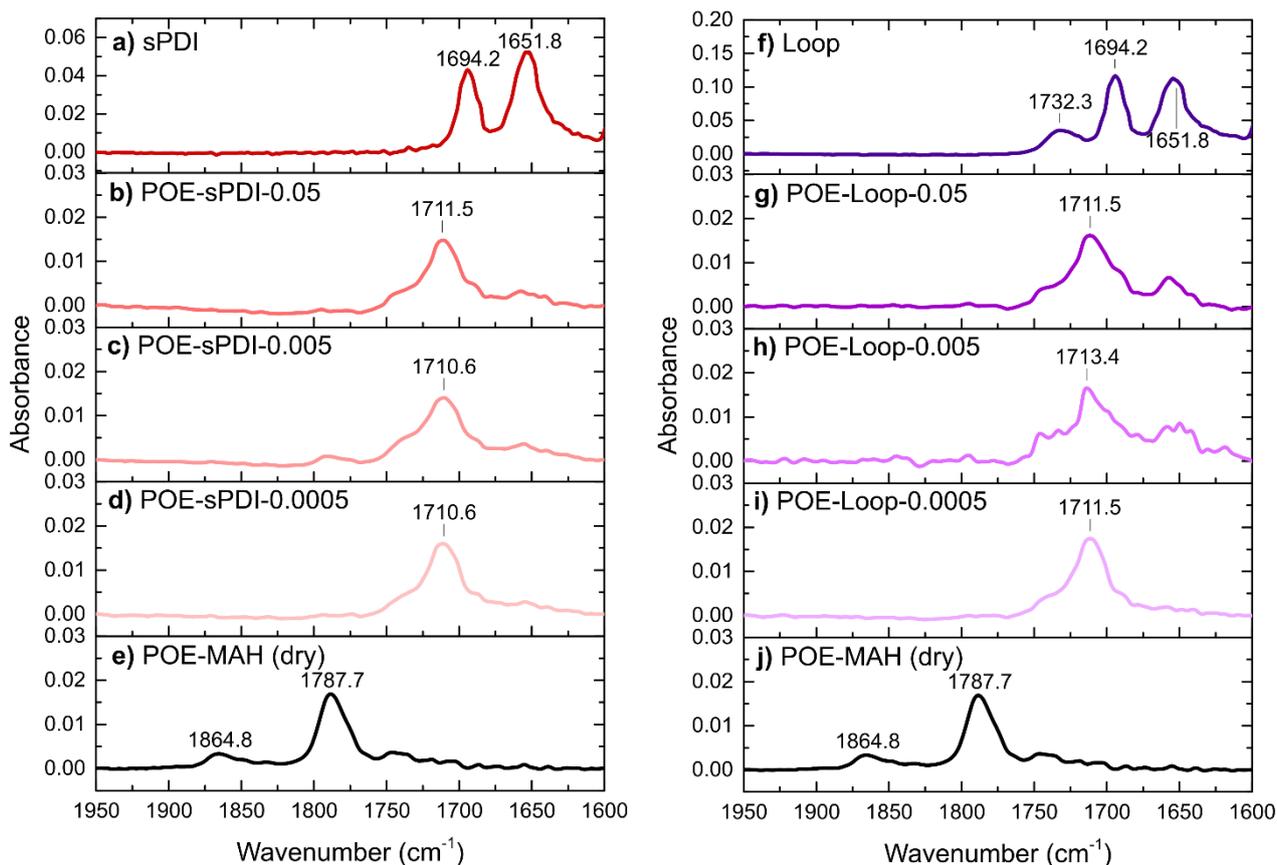


Figure S3. IR spectra, zoomed in on the C=O stretching region, for cross-linker **sPDI** (a), **POE-sPDI-0.05** (b), **POE-sPDI-0.005** (c), **POE-sPDI-0.0005** (d), **POE-MAH** (dried after thermal treatment) (e), cross-linker **Loop** (f), **POE-Loop-0.05** (g), **POE-Loop-0.005** (h), **POE-Loop-0.0005** (i). For convenience, the spectrum of **POE-MAH** (dried after thermal treatment) is repeated in (j). The stretching vibration at 1710.6 – 1711.5 cm^{-1} of the carboxylic acid in the hemi-ester of MAH is labelled in the spectra of **POE-sPDI-X** (b-d) and **POE-Loop-X** (g-i). The corresponding ester stretch is present as a shoulder of the carboxylic acid stretch at ca. 1740 cm^{-1} .

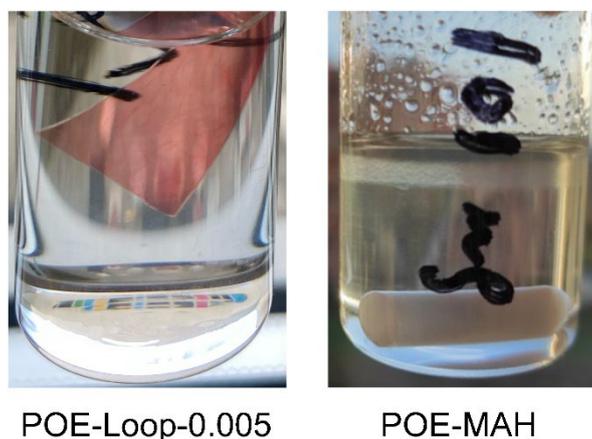


Figure S4. Swelling tests in chloroform to demonstrate the occurrence of the crosslinking reaction in **POE-sPDI**. Left vial: **POE-Loop-0.005** which is swollen and not dissolved in the solvent. Right vial: **POE-MAH** dissolved in chloroform.

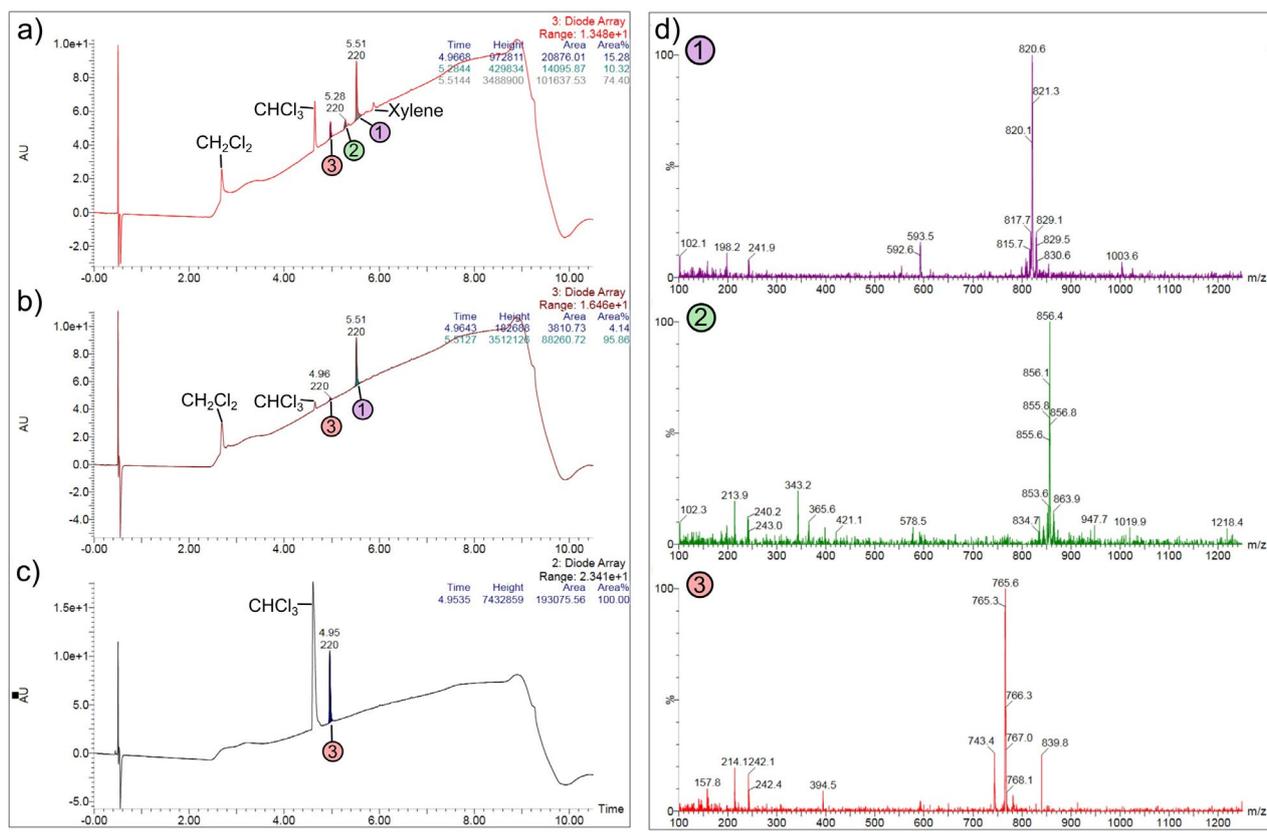


Figure S5. Acid stability test for **Loop**. UPLC chromatograms of reaction mixture obtained after heating **Loop** to reflux in chloroform for 48 h in the presence of p-TSA (a), of **Loop** (b) and of **sPDI** (c). d) Mass spectra for peaks in chromatogram a). (1) corresponds to unreacted **Loop** ([**Loop**+2Na]²⁺), and (3) corresponds to **sPDI** ([**sPDI**+Na]⁺). (2) may correspond to **Loop** in which the diimides have been hydrolyzed to the corresponding imide and carboxylic acid ([**Loop**+2Na+4H₂O]²⁺)

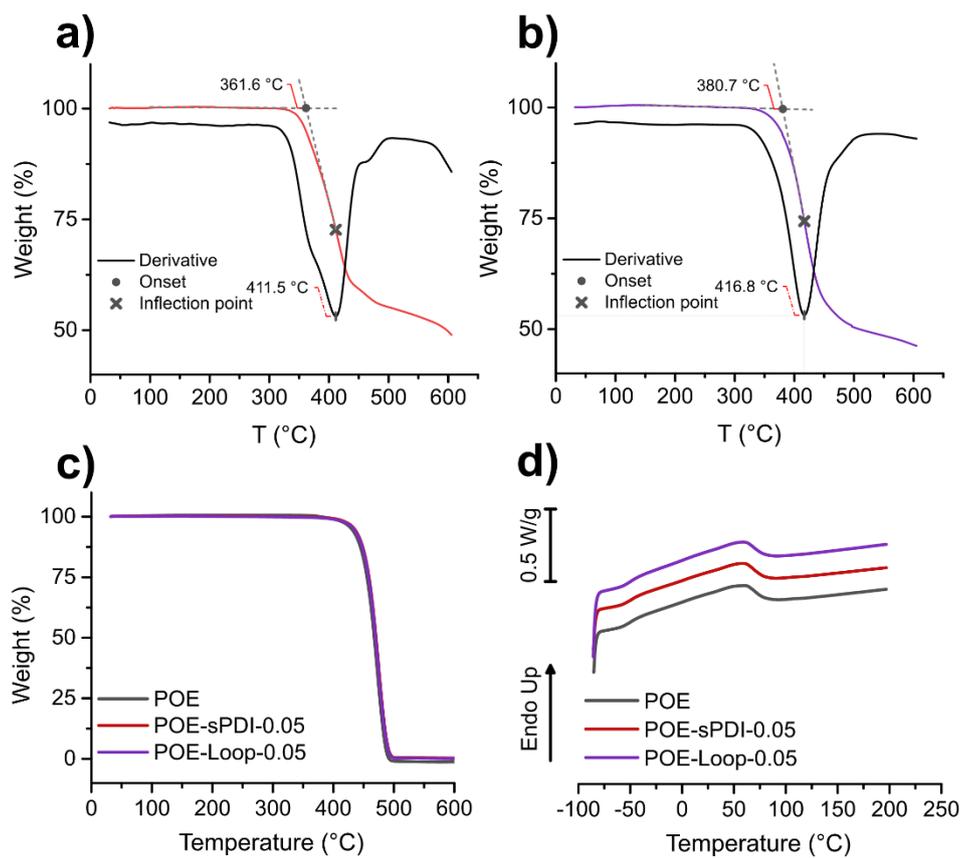


Figure S6. TGA curves of the **sPDI** (a) and **Loop** (b) crosslinkers, and for **POE** and **POE-X-0.05** (c). DSC curves for **POE** and **POE-X-0.05** (d).

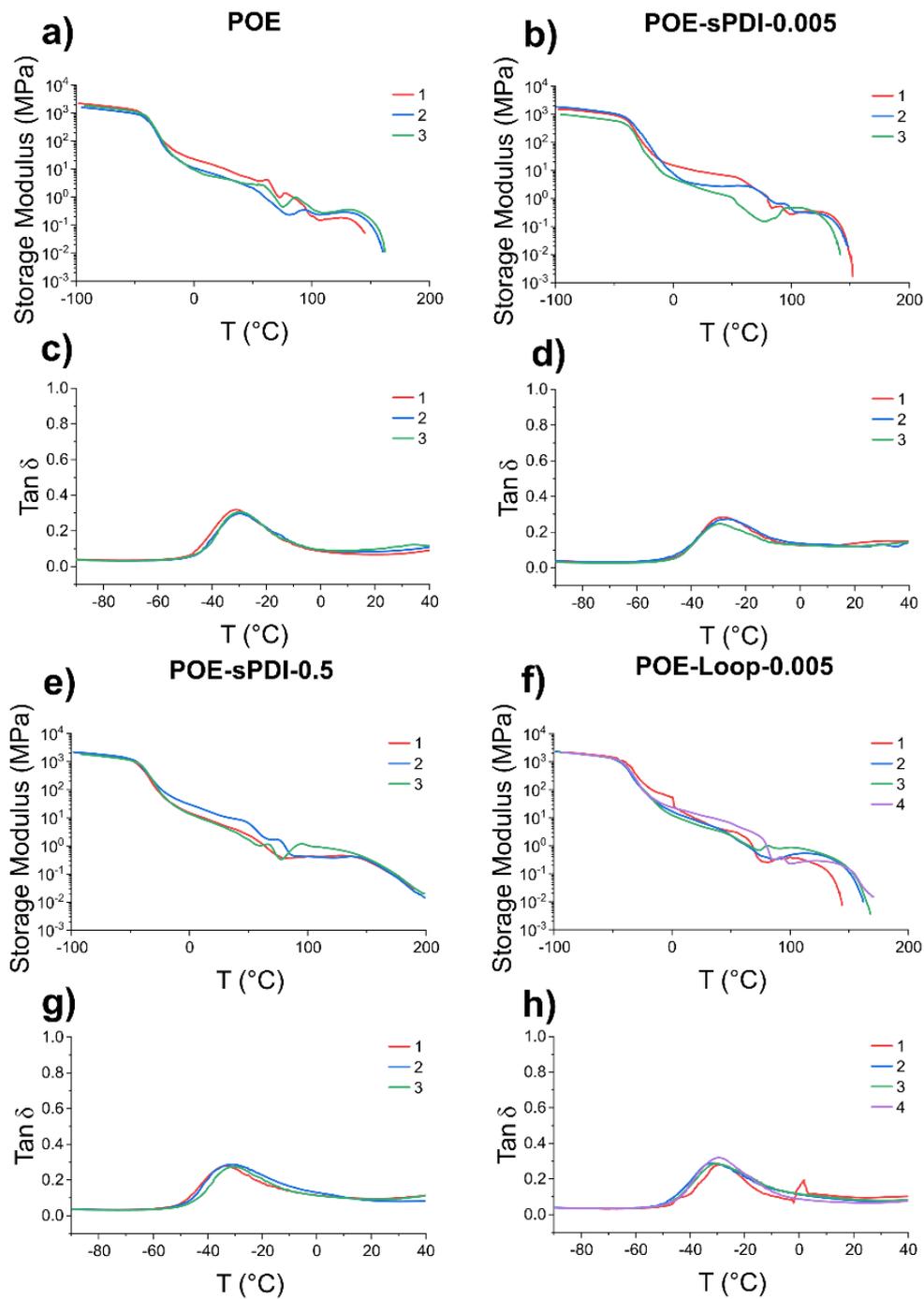


Figure S7. DMA and tan delta curves for **POE** (a,c), **POE-sPDI-0.005** (b,d), **POE-sPDI-0.5** (e,g) and **POE-Loop-0.005** (f,h). Three samples of each material were characterized.

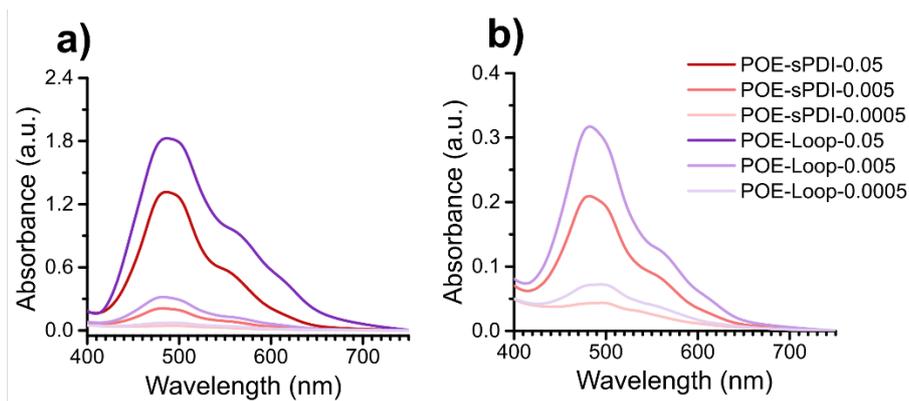


Figure S8. (a) UV-vis absorbance of **POE-sPDI** and **POE-Loop** containing different concentrations of **sPDI** or **Loop** as crosslinker, with a zoom-in at lower absorbance (b).

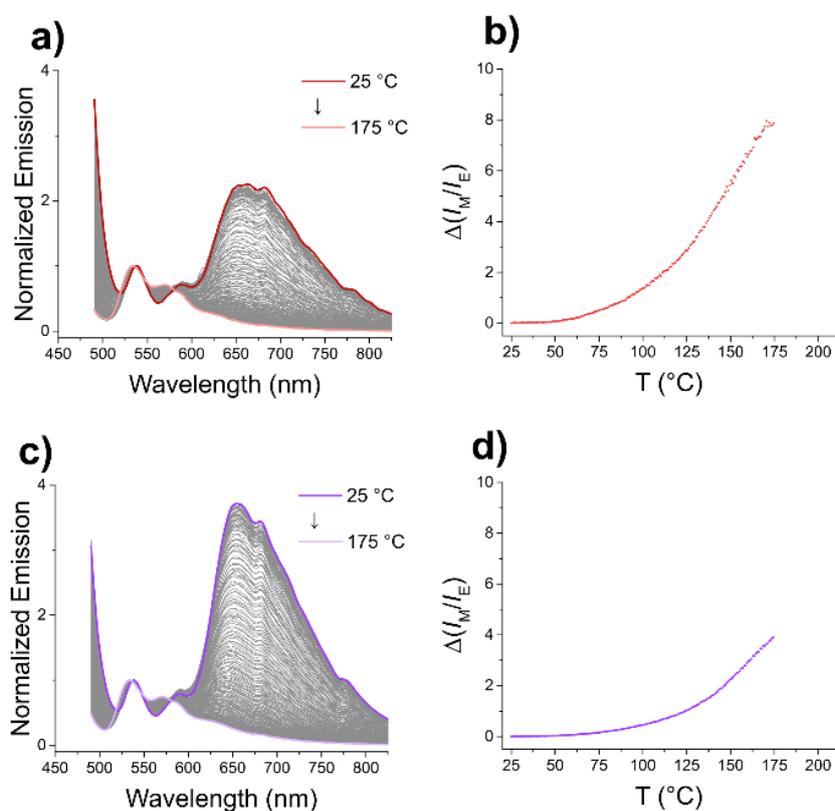


Figure S9. (a,b) Changes in fluorescence spectra of **POE-sPDI-0.005** upon heating (a) and corresponding changes in monomer-to-excimer emission intensity ratio (normalized by peak intensity of monomer band) with temperature (b). (a,b) and (c,d) represent two independent runs. (c,d) Changes in fluorescence spectra of **POE-Loop-0.005** upon heating (c) and corresponding changes in monomer-to-excimer emission intensity ratio with temperature (d). The data in Figure 4 and Figure S9 represent two independent runs.

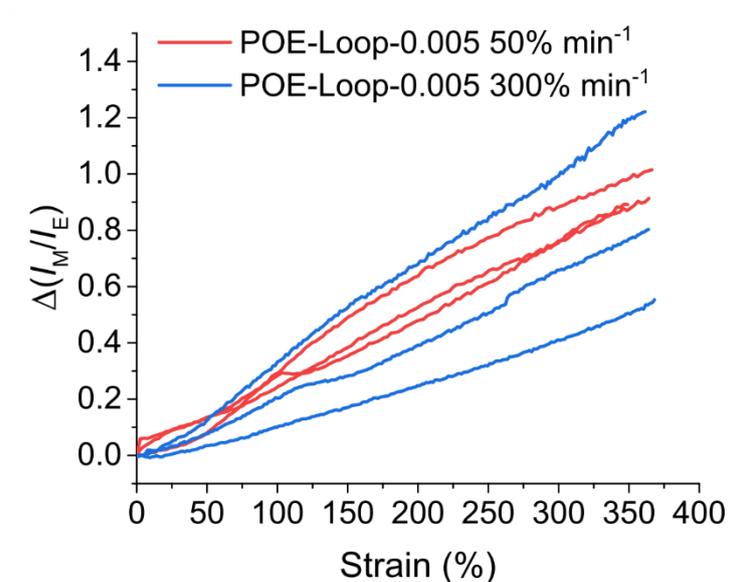


Figure S10. Change in monomer-to-excimer emission intensity ratio, $\Delta(I_M/I_E)$ with respect to $(I_M/I_E)_0$ at strain 0% for **POE-Loop-0.005** with increasing applied tensile strain, for strain rates of 50 and 300 % min^{-1} (3 independent runs per strain rate).

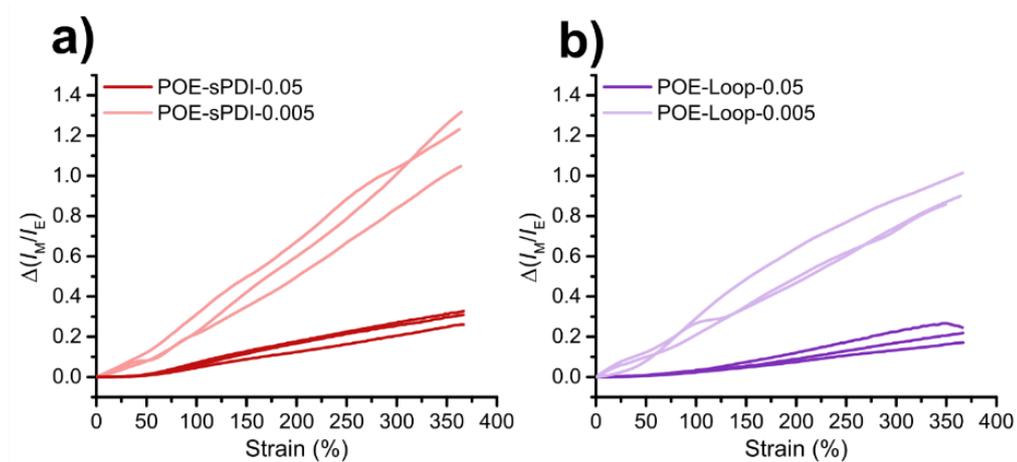


Figure S11. Change in monomer-to-excimer emission intensity ratio, $\Delta(I_M/I_E)$ with respect to $(I_M/I_E)_0$ with increasing applied tensile strain for **POE-sPDI-0.05** and **POE-sPDI-0.005** (a) and **POE-Loop-0.05** and **POE-Loop-0.005** (b) (3 independent runs for each composition).

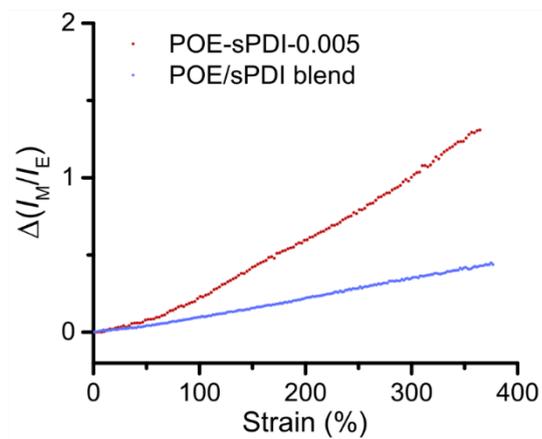


Figure S12. Change in monomer-to-excimer emission intensity ratio, $\Delta(I_M/I_E)$ with respect to $(I_M/I_E)_0$ with increasing applied tensile strain for **POE-sPDI-0.005** and a sample containing physically dispersed sPDI crosslinker in POE for the same concentration of sPDI.

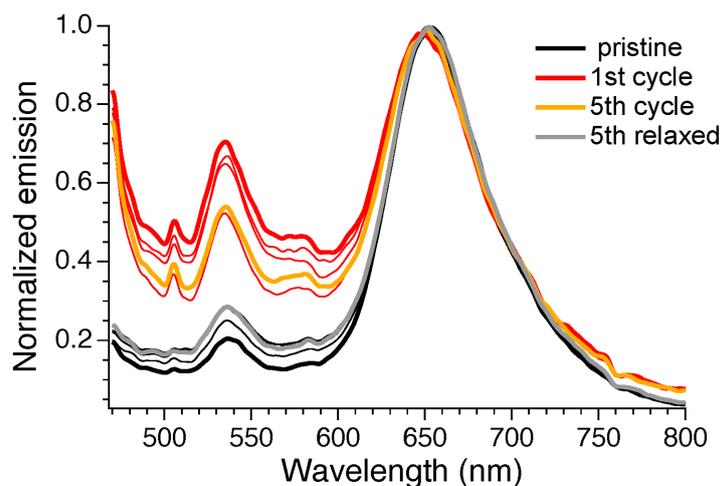


Figure S13. Normalized fluorescence spectra of **POE-Loop-0.005** subjected to 5 cycles to 150% tensile strain. For each cycle, the spectrum was recorded at 150% strain (red or orange) and after subsequent relaxation to 0% strain (black or grey). The spectra at 150% strain in the first and fifth cycles are highlighted (red and orange bold, respectively), as well as the spectra at 0% strain at the start and end of the test (black and gray bold, respectively). The spectra are normalized by the intensity of the excimer band at 650 nm.

Table S1. Monomer-to-excimer emission intensity ratio I_M/I_E calculated from the fluorescence spectra of POE-Loop-0.005 subjected to five cycles of tensile strain to 150% shown in Figure S13.

Cycle	I_M/I_E	
	0% strain	150% strain
1	0.20459	0.7045
2	0.25071	0.66689
3	0.28292	0.64724
4	0.28487	0.5232
5	0.28441	0.53898
end	0.28487	-

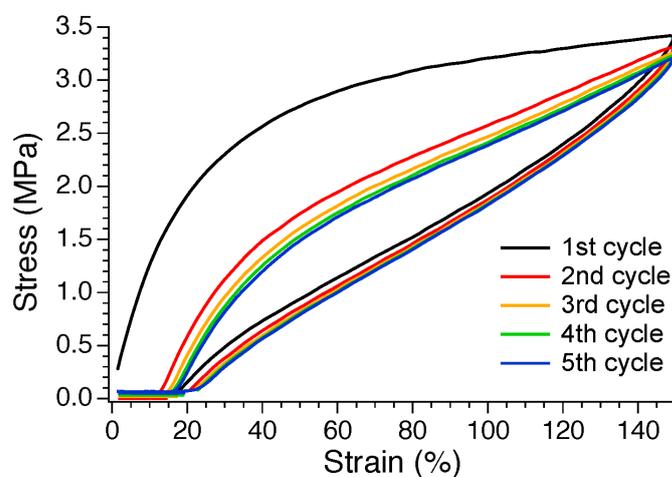


Figure S14. Corresponding stress-strain plot for the cyclic tensile test in Figure S13. Deformation to 150% strain is not fully reversible.

Materials

Poly(ethylene-co-octene) functionalized on the aliphatic segment with maleic anhydride (POE-MAH) was kindly supplied by Dow Chemical Company, (USA). The product exhibits a degree of functionalization of grafted anhydride equal to 1 wt.%, a density of 0.88 g cm^{-3} and a Melt Flow Rate ($190^\circ\text{C}/2.16\text{kg}$) of $3.7 \text{ g}/10 \text{ min}$ (ASTM D1238). 2-(2-(2-(2-Aminoethoxy)ethoxy)ethoxy)ethanol was purchased from abcr GmbH (Germany). N,N-Dimethylformamide, and pyridine were purchased from Acros Organics. Ammonium chloride was purchased from Roth. The remaining chemicals were obtained from Sigma-Aldrich. All chemicals were used without further purification. The syntheses of perylene diimide derivatives were carried out employing anhydrous and inert conditions according to published protocols.

Synthesis of Perylene Diimide (PDI) Derivatives

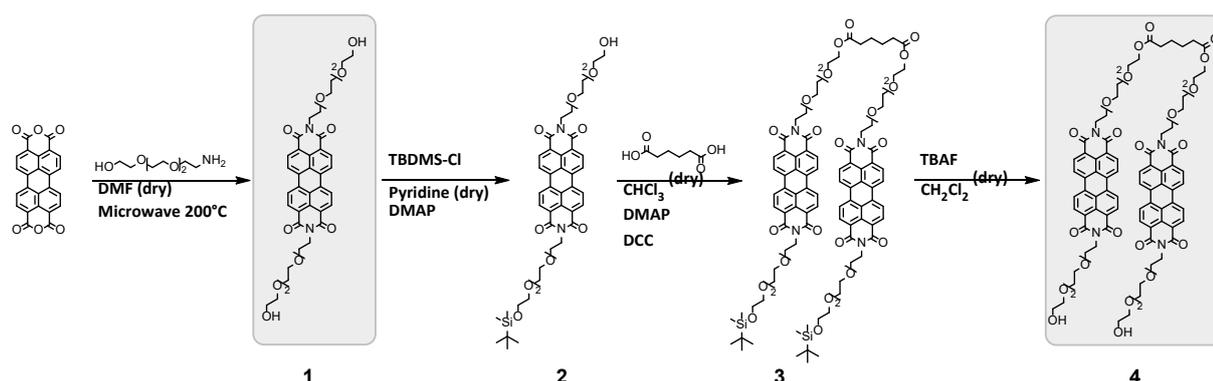


Figure S14. Synthetic pathway to prepare single perylene diimide (sPDI) probe (**1**), and **Loop**, containing two perylene diimide moieties covalently connected by an adipic acid linker (**2**).

Synthesis of 1. Perylenetetracarboxylic dianhydride (1.60 g, 4.08 mmol, 1 eq.) was suspended in dry DMF (68 mL) and 2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethanol (1.58 g, 1.48 mL, 8.18 mol, 2 eq.) was added. The mixture was divided into four aliquots and each was subjected to 30 min of microwave irradiation at 200°C . The four portions were then combined, the solvent was removed in vacuo and the crude product was purified by flash column chromatography using gradient elution (DCM to DCM:MeOH 9:1 v/v) to obtain **1** as a dark red solid (2.44 g, 3.28 mmol, 80.5%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.65 (d, $J=7.9$ Hz, 4H), 8.56 (d, $J=8.0$ Hz, 4H), 4.48 (t, $J=6.0$ Hz, 4H), 3.88 (t, $J=6.0$ Hz, 4H), 3.81–3.26 (m, 26H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.46, 134.52, 131.44, 129.35, 126.28, 123.27, 123.14, 72.65, 70.78, 70.49, 70.29, 68.14, 61.89, 39.52.

Synthesis of 2. Following a previous protocol by Wang et al., **1** (1.20 g, 1.62 mmol, 1 eq.) was dissolved in pyridine and 4-(dimethylamino)pyridine (0.061 g, 0.50 mmol, 0.3 eq.) and tert-butyldimethylsilyl chloride (0.38 g, 2.52 mmol, 1.6 eq.) were added. The mixture was stirred overnight followed by the removal of the solvent in vacuo. The crude mixture was purified by column flash column chromatography using gradient elution (DCM to DCM:MeOH 9:1 v/v) to obtain **2** as a brown solid (0.64 g, 0.75 mmol, 46.3%). The reaction was repeated twice (average yield 34.3%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.50 (d, $J=7.9$, 4H), 8.34 (d, $J=8.0$ Hz, 4H), 4.46 (t, $J=6.0$, Hz, 4H), 3.88 (t, $J=6.0$ Hz, 4H), 3.80–3.47 (m, 25H), 0.91 (s, 9H), 0.09 (s, 6H).

Synthesis of 3. Following a previous protocol by Chen et al., **2** (0.71 g, 0.83 mmol, 2 eq.) and 4-(dimethylamino)pyridine (0.11 g, 0.90 mmol, 2 eq.) were added to a Schlenk flask under nitrogen atmosphere and dissolved in dry CHCl_3 (12 mL). Adipoic acid (0.061 g, 0.42 mmol, 1 eq.) was separately dissolved in dry DMF (3 mL) and added to the mixture, followed by drop-wise addition of a solution of N,N'-dicyclohexylcarbodiimide (0.31 g 1.50 mmol, 3.6 eq.) in dry CHCl_3 (3 mL). The mixture was stirred for 48 h

followed by the removal of the solvent in vacuo, and the crude material subjected to flash column chromatography using gradient elution (DCM to DCM:MeOH 9:1 v/v) to obtain **3** as a dark red powder (0.55 g, 0.30 mmol, 71.4%).

^1H NMR (400 MHz, CDCl_3) δ 8.35 (dd, $J=6.5, 8.0$ Hz, 8H), 8.12 (dd, $J=8.2, 7.1$ Hz, 8H), 4.44 (q, $J=6.1$ Hz, 8H), 4.23–4.16 (m, 4H), 3.89 (td, $J=6.1, 4.4$ Hz, 8H), 3.82–3.55 (m, 40H), 3.51 (t, $J=5.5$ Hz, 4H), 2.57–2.09 (m, 4H), 1.86–1.39 (m, 4H), 0.86 (s, 18H), 0.03 (s, 12H).

Synthesis of 4. In a Schlenk flask under nitrogen atmosphere, **3** (0.51 g, 0.28 mmol, 1 eq.) was dissolved in dry DCM (5 mL) and tetrabutylammonium fluoride (2.8 mL, 1 M in THF, 10 eq.) was added. The mixture was stirred at ambient temperature overnight, before washing once with saturated aqueous NH_4Cl solution and three times with saturated aqueous NaCl solution. The organic phase was isolated and dried over sodium sulfate, and the solvent was removed in vacuo. The crude mixture was purified by flash column chromatography (DCM to DCM:MeOH 9:1 v/v) to obtain **4** as a dark red solid (0.31 g, 0.19 mmol; 67.9%).

^1H NMR (400 MHz, CDCl_3) δ 8.27 (dd $J=14.0, 7.2$ Hz, 8H), 8.01 (s, 8H), 4.42 (q, $J=6.5$ Hz, 8H), 4.28–4.07 (m, 4H), 3.90 (td, $J=6.0, 2.5$ Hz, 8H), 3.83–3.74 (m, 8H), 3.73–3.14 (m, 38H), 2.52–2.21 (m, 4H), 1.73–1.47 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 173.29, 163.0, 162.90, 133.74, 133.71, 130.91, 130.81, 128.74, 128.69, 125.49, 122.87, 122.85, 122.71, 72.56, 70.77, 70.70, 70.66, 70.63, 70.60, 70.37, 70.17, 70.14, 69.15, 68.02, 67.93, 63.53, 61.77, 39.38, 33.79, 24.32.

Purification of Polymeric Matrices

POE-MAH was dissolved in CHCl_3 and reprecipitated by dropwise addition to stirred MeOH (CHCl_3 :MeOH = 1: 20 v/v). The polymer was recovered by filtration and dried under vacuum. After purification, the polymer was dried for 4 h at 170 °C under vacuum to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydrides. Thermal treatment was monitored by FT-IR in ATR mode (Figure 1.4).

Preparation of Covalently Functionalized Polymeric Films

Typically, 1 g POE-MAH was dissolved in 30 mL of CHCl_3 at 45-50 °C and the solution was allowed to cool to room temperature. The required amounts of fluorescent probe and catalyst (5 mol.% *p*-toluenesulfonic acid monohydrate (PTSA) relative to the molar amount of MAH groups), were added to the solution. After stirring for 30', the solution was poured into a Teflon Petri dish with a diameter of 6 cm and the solvent was evaporated at room temperature in a well-ventilated hood. The resulting materials were compression-molded between Teflon sheets in a Collin press at 75 °C for 90 min at a pressure of 250 bar. The reaction was monitored by FT-IR spectroscopy in ATR mode and by dynamic mechanical thermal analysis (DMTA).

Preparation of Blend Polymeric Film

Typically, 1 g of POE-MAH was dissolved in CHCl_3 at 45-50 °C and the solution allowed to room temperature. The required amount of fluorescent probe was added to the solution. After 30', the solution was poured into a Teflon Petri dish and the solvent evaporated at room temperature. The resulting material was compression-molded between Teflon sheets in a Collin press at 75 °C for POE-MAH for 10 min at 250 bar (thickness ca. 150 μm).

Methods

NMR spectroscopy was carried out at 297.2 K on a Bruker Avance DPX 400 spectrometer at frequencies of 400.19 MHz for ^1H nuclei and 100.63 MHz for ^{13}C nuclei. Spectra were referenced to the residual solvent peak of CHCl_3 . Spectra were processed with the MestReNova software suite and all chemical shifts (δ) are reported in parts per million (ppm) with coupling constant in Hz.

FT-IR measurements were performed on a Perkin Elmer Spectrum 65 spectrometer in ATR mode between 500 and 4000 cm^{-1} (3 scans per sample).

Steady-state fluorescence spectroscopy in solution or solid-state was carried out with a Horiba Fluorolog 3 spectrometer with right angle illumination equipped with a 450 W Xenon light source for excitation and a FL-1030-UP photomultiplier as detector. Fluorescence changes in polymer films as a function of temperature or mechanical strain were recorded using an Ocean Optics USB 4000 spectrometer connected to an Ocean Optics LS-450 LED light source with an excitation wavelength of $\lambda_{\text{ex}} = 470\text{ nm}$ and an Ocean Optics QR230-7-XSR SMA 905 optical fiber. Samples were placed on top of a reflective metal block as substrate, the optical fiber was oriented with an angle of 45° relative to the surface at a distance of ca. 2 mm, and the emission spectrum was measured. Spectra were recorded before, and during the application of mechanical stress, and fluorescence data were recorded at an acquisition rate of 0.5 Hz (acquisition every 2 seconds) using the Stream Basic software.

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 2 STAR system operated under a nitrogen atmosphere with heating and cooling rates of $10\text{ }^\circ\text{C min}^{-1}$ in a temperature range from -80 to $180\text{ }^\circ\text{C}$. Two heating and cooling cycles were measured with heating and cooling rates of $10\text{ }^\circ\text{C min}^{-1}$.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC 1 STAR system from 25 to 600°C in air flow with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Dynamic mechanical thermal analysis (DMTA) was performed with a TA Instruments DMA Q800 over a temperature range of $-100\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ with a heating rate of $3\text{ }^\circ\text{C min}^{-1}$ at a frequency of 1 Hz and an amplitude of $3\text{ }\mu\text{m}$.

Stress-strain experiments were conducted on rectangular samples with dimensions of 40×5.5 (length \times width). The experiments were carried out on a Linkam TST350 micro tensile stage equipped with a 20 N load cell at a strain rate of $50\text{ }\% \text{ min}^{-1}$ or $300\text{ }\% \text{ min}^{-1}$ and Linksys32 software was used to acquire the data. To simultaneously record fluorescence spectra, an Ocean Optics USB 4000 spectrometer was used as described above.

Heating stage for temperature-dependent fluorescence measurements was carried out using a Linkam LS350 heating stage system. To simultaneously record fluorescence spectra, an Ocean Optics USB 4000 spectrometer was used as described above.

The thickness and the width of the polymeric films were measured with a micrometer device and with a caliper respectively.

Flash column chromatography was performed on a Biotage Isolera One flash column chromatography system with a UV-vis detector.

An Initiator 8 EXP Microwave system equipped with an Initiator Robot 8 was used for microwave reactions.

Fluorescence microscopy images were acquired at 20x magnification using an Olympus BX51 microscope equipped with an Olympus DP72 high-resolution camera. The samples were imaged in reflectance mode using an X-Cite Series 120-Q Mercury vapor short arc lamp as the excitation source. Images were recorded with a blue excitation/green emission filter (λ_{ex} : 480/40 nm; λ_{em} : 535/50 nm, Olympus U-MF2), a blue excitation/red emission filter (λ_{ex} : 469/35 nm, Thorlabs MF469-35; λ_{em} : 620/52 nm, Thorlabs MF620-52), where the numbers indicate the wavelength of peak transmission and the full width at half maximum, respectively, or a UV

excitation/ wideband emission filter ($\lambda_{\text{ex}} = 330\text{-}385$ nm; $\lambda_{\text{em}} = 420\text{-}900$ nm, Olympus U-MWU2). A standard white diffuser was used as a white reference sample.

Photographs were taken with a Xiaomi mobile phone, 50MP 1/1.56" sensor, 2 μm pixels, f/1.88 aperture lens, OIS, AF.