

Supporting Information for

Mechanochromic polymer blends made with an excimer-forming telechelic sensor molecule

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1. Supporting Data

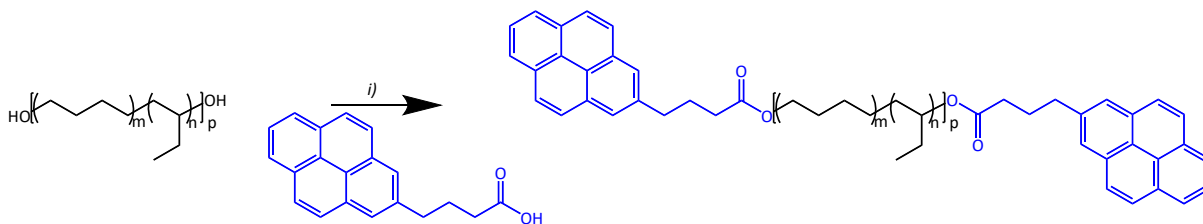


Figure S1. Scheme of the synthesis of the excimer-forming, pyrene-terminated poly(ethylene-co-butylene) (**Py-PEB**). **Py-PEB** was prepared from 1-pyrenebutyric acid and dihydroxy-terminated poly(ethylene-co-butylene) (OH-PEB) ($M_n = 3100 \text{ g mol}^{-1}$). *Reagents and conditions:* *i)* DCC, DMAP, CH_2Cl_2 , rt, N_2 , 28 h, 32%.

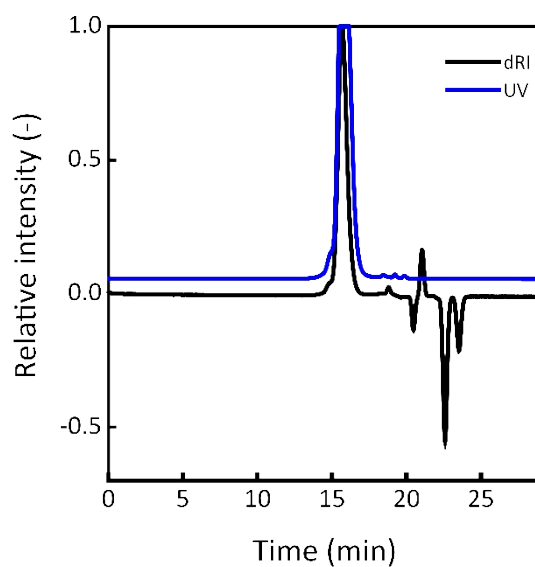


Figure S2. Size-exclusion chromatography (SEC) traces of **Py-PEB** detected by refractive index (dRI) and UV-Vis absorption detectors. Since the PEB backbone does not absorb light in the UV-vis regime, the overlap of the two traces shows that the pyrene moieties are covalently attached to the telechelic PEB core.

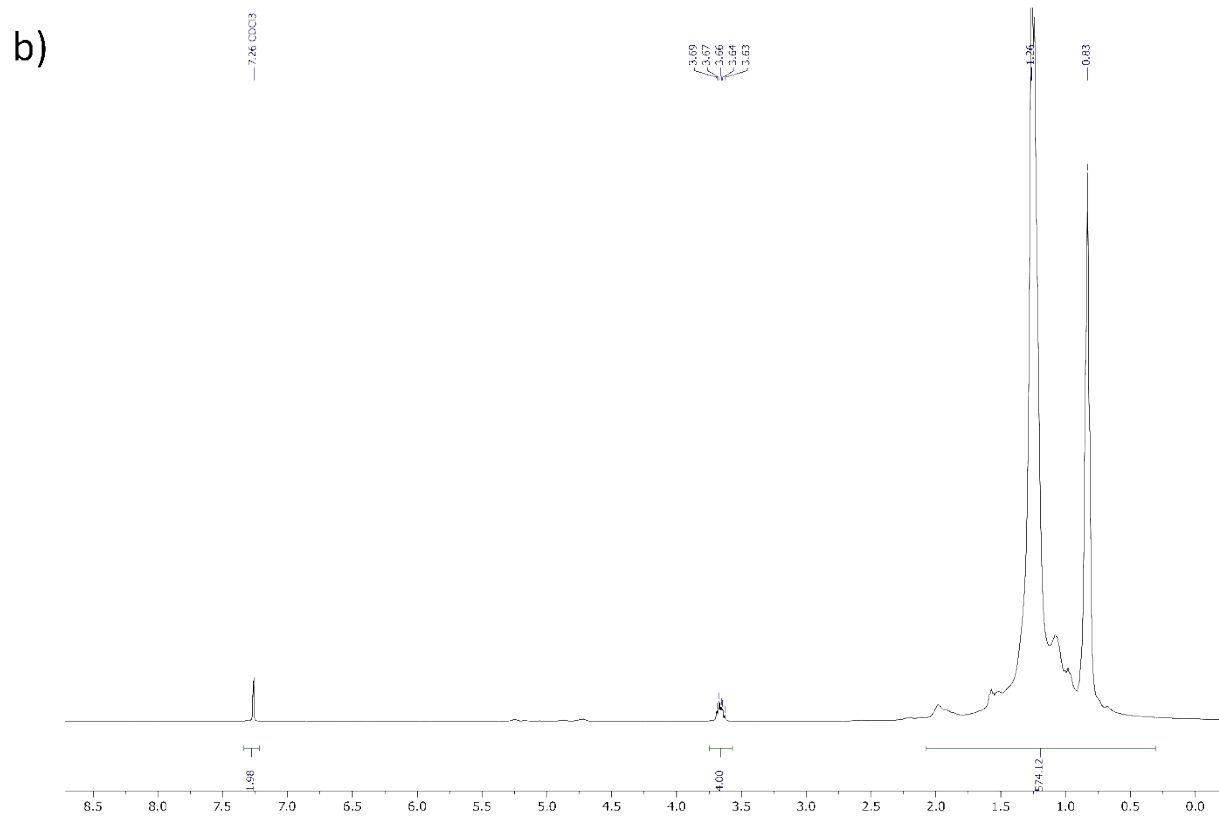
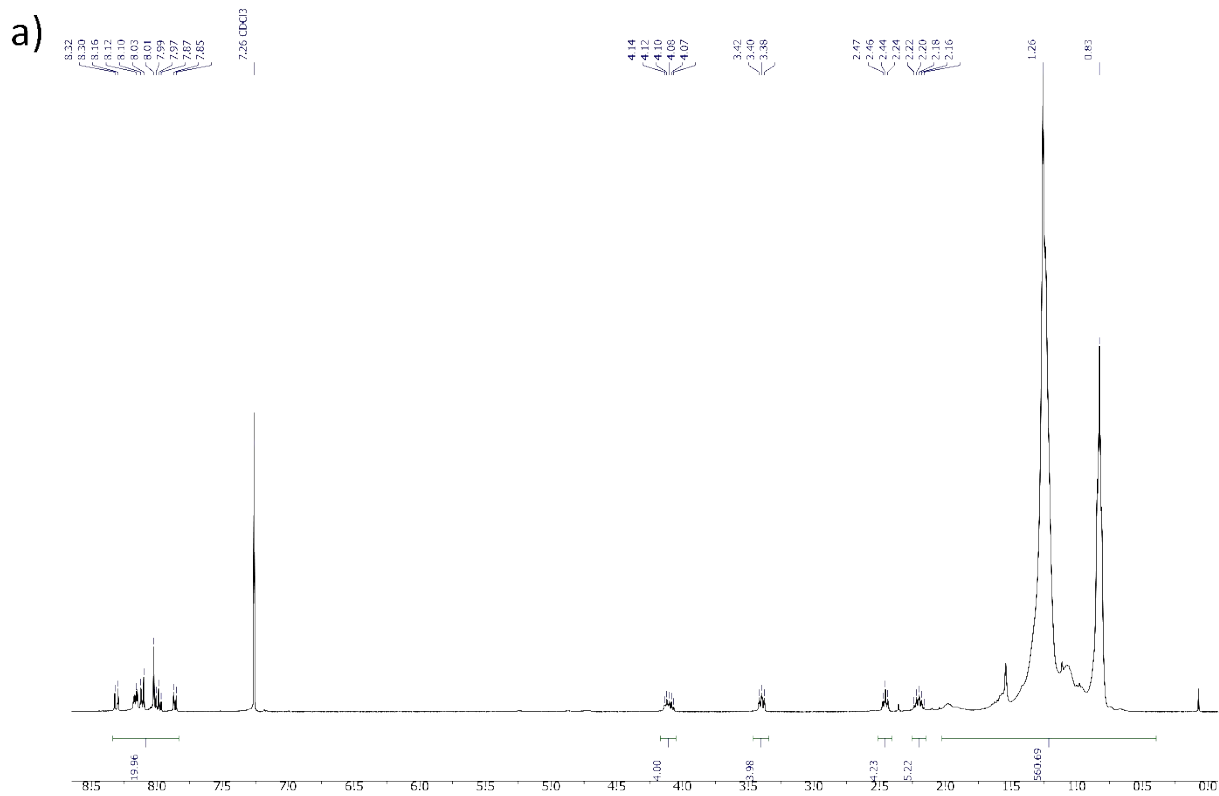


Figure S3a,b. a) ¹H-NMR spectrum of Py-PEB; b) ¹H-NMR spectrum of OH-PEB recorded in CDCl₃.

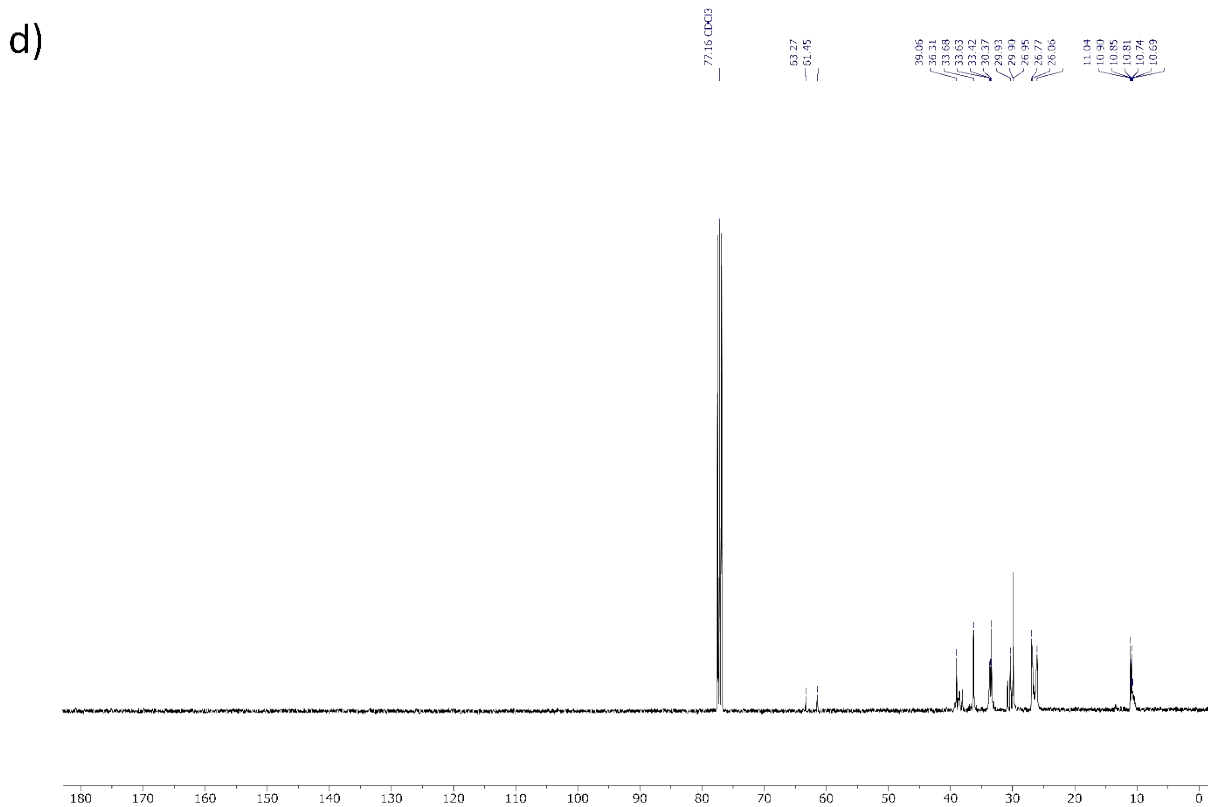
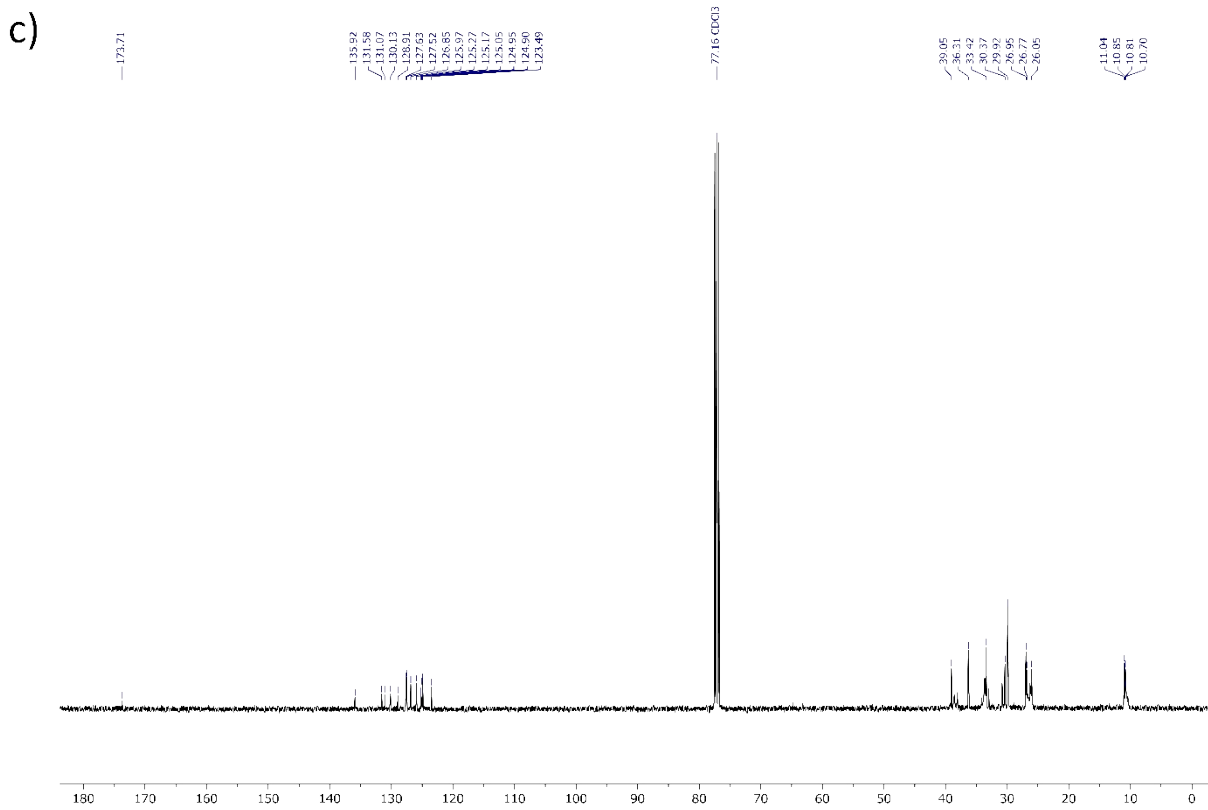


Figure S3c,d. c) ^{13}C -NMR spectrum of Py-PEB; d) ^{13}C -NMR spectrum of OH-PEB recorded in CDCl_3 .

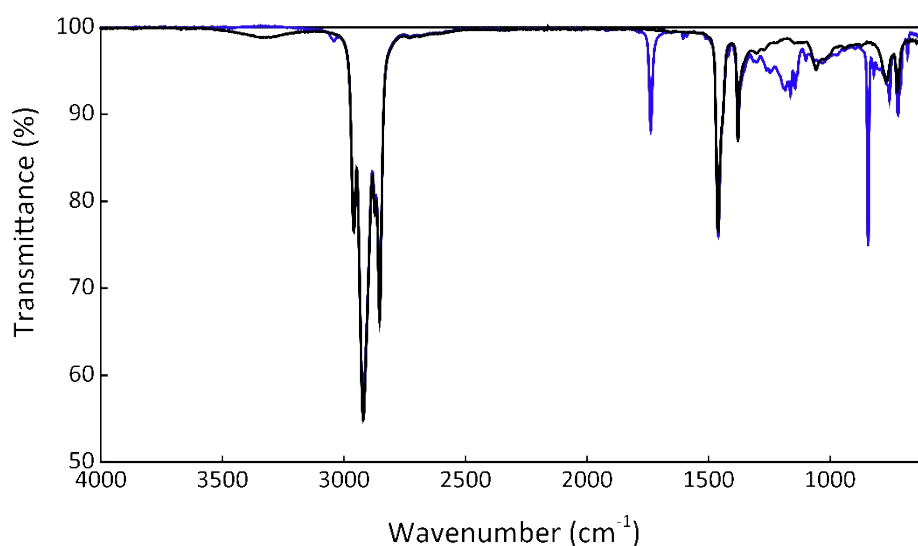


Figure S4. FTIR spectra of **Py-PEB** (blue) and **OH-PEB** (black).

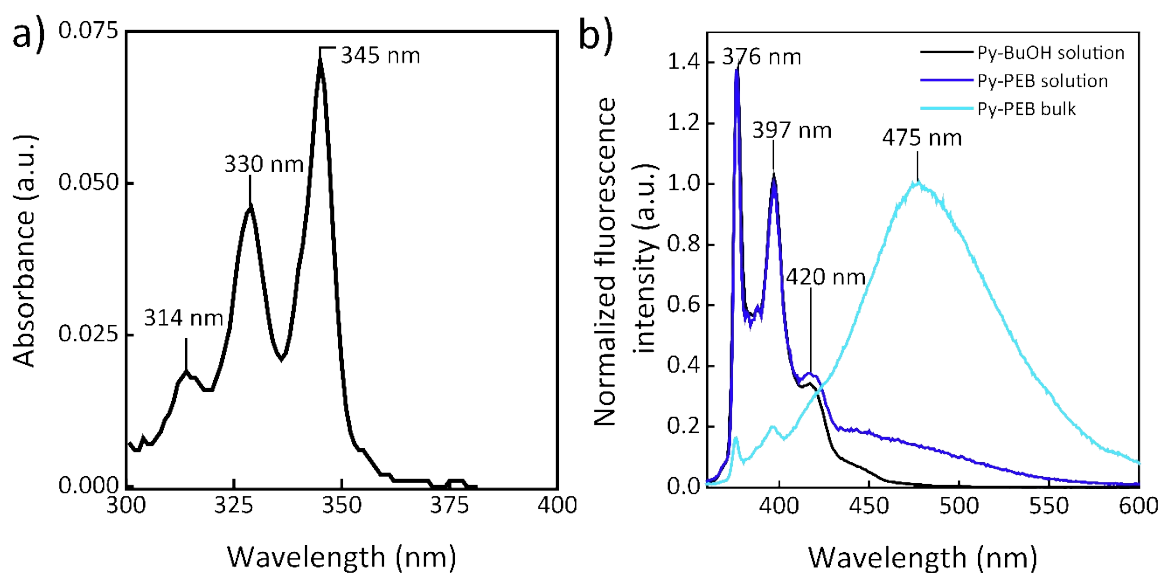


Figure S5. a) UV-Vis absorption spectrum of **Py-PEB** in toluene ($c = 1 \mu\text{mol L}^{-1}$). b) Photoluminescence spectra of a toluene solution of the low-molecular weight model compound 1-pyrenebutanol ($c = 2 \mu\text{mol L}^{-1}$, black), a **Py-PEB** solution in toluene ($c = 1 \mu\text{mol L}^{-1}$, blue), and **Py-PEB** in the liquid bulk state (cyan). The excitation wavelength was, in all cases, 310 nm. The emission spectra show exclusively monomer (1-pyrenebutanol solution), predominantly monomer (**Py-PEB** solution), and predominantly excimer (bulk **Py-PEB**) emission.

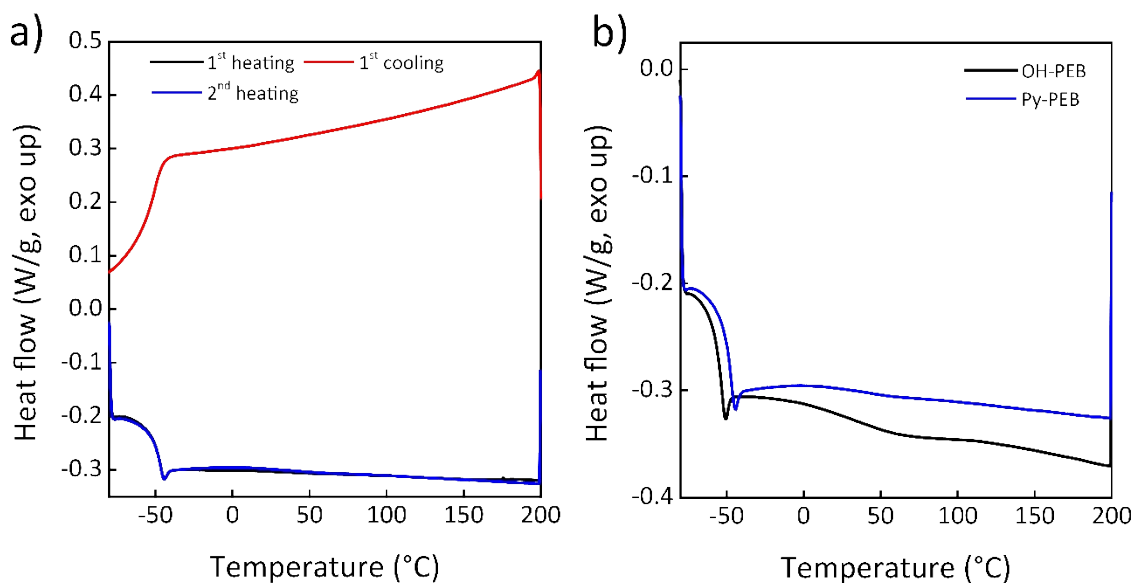


Figure S6. a) Differential scanning calorimetry (DSC) traces (first and second heating and first cooling scans) of **Py-PEB**. The material is completely amorphous, with a T_g at ca. -44°C . b) DSC traces (second heating) of the parent OH-PEB (black) and **Py-PEB** (blue). The curves show that the T_g of **Py-PEB** (ca. -44°C) is slightly higher than the T_g of OH-PEB (ca. -50°C). All DSC traces were acquired at heating and cooling rates of $10^\circ\text{C min}^{-1}$.

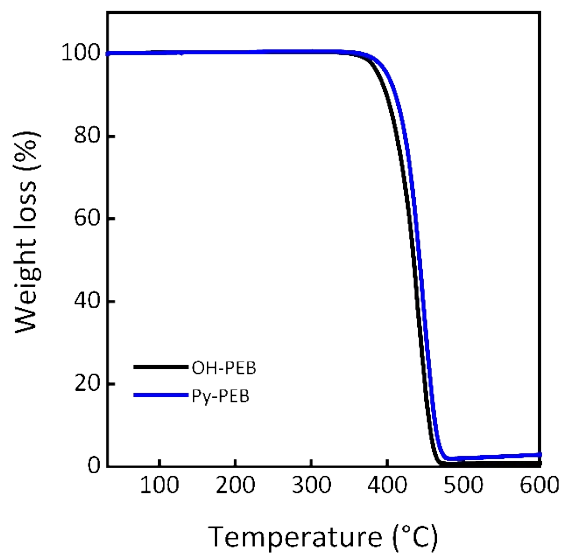


Figure S7. Thermogravimetric analysis (TGA) traces of **Py-PEB** (blue) and the parent OH-PEB (black). The pyrene-functionalized telechelic shows a slightly higher onset temperature of thermal degradation (326°C) than the parent OH-PEB (318°C). The traces were acquired at a heating rate of $10^\circ\text{C min}^{-1}$.

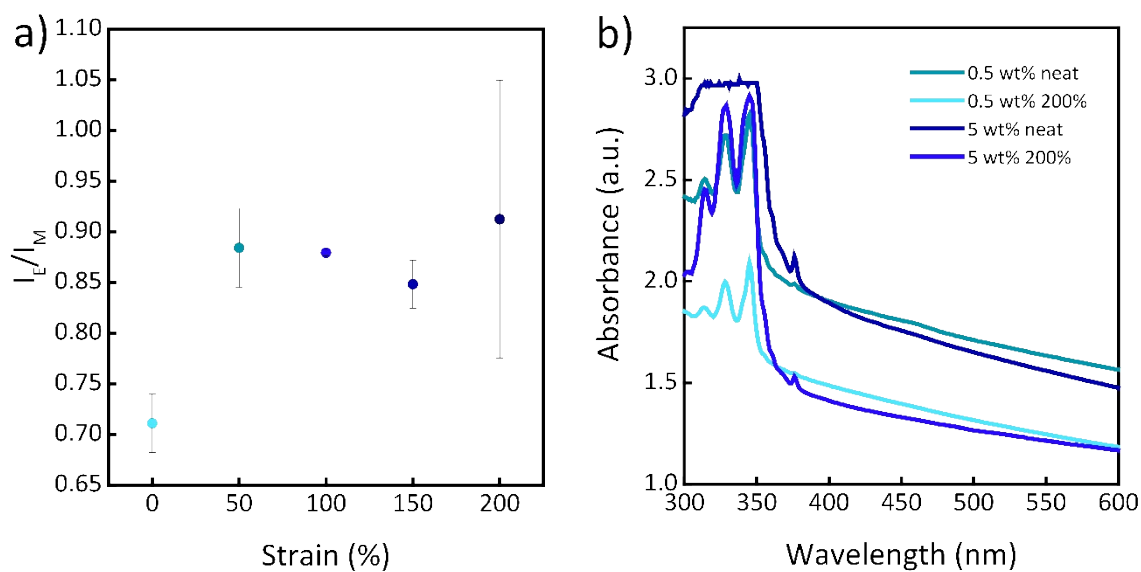


Figure S8. a) Plot of the excimer-to monomer intensity ratio I_E/I_M of PI/Py-PEB₅ film samples, stretched to 200% strain at a strain rate of 50% min⁻¹. The excitation wavelength was 310 nm. b) UV-Vis absorbance spectra of PI/Py-PEB_{0.5} and PI/Py-PEB₅ film samples. A higher level of light scattering around 397 nm (I_M) could explain why the neat samples show lower I_E than the stretched samples.

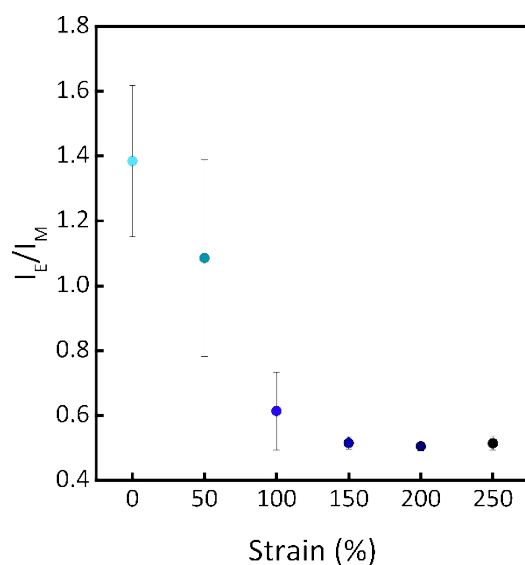


Figure S9. Plot of the excimer-to-monomer intensity ratio I_E/I_M of PCL/Py-PEB₁ film samples, stretched to 250% strain at a strain rate of 50% min⁻¹. The excitation wavelength was 310 nm.

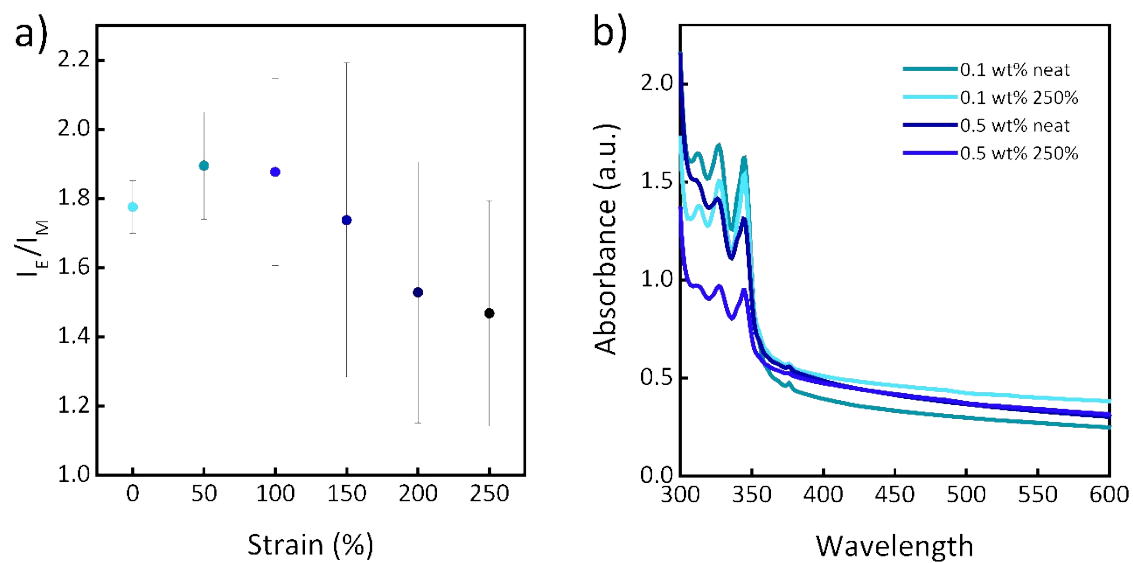


Figure S10. a) Plot of the excimer-to monomer intensity ratio I_E/I_M of PU/Py-PEB_{0.2} film samples, stretched to 250% strain at a strain rate of 50% min⁻¹. The excitation wavelength was 310 nm. b) UV-Vis absorbance spectra of PU/Py-PEB_{0.1} and PU/Py-PEB_{0.5} film samples. Scattering of light at 397 nm here does not vary greatly between neat and stretched samples. The origin of the increase in I_E between 0 and 50% strain is still unclear for these samples.

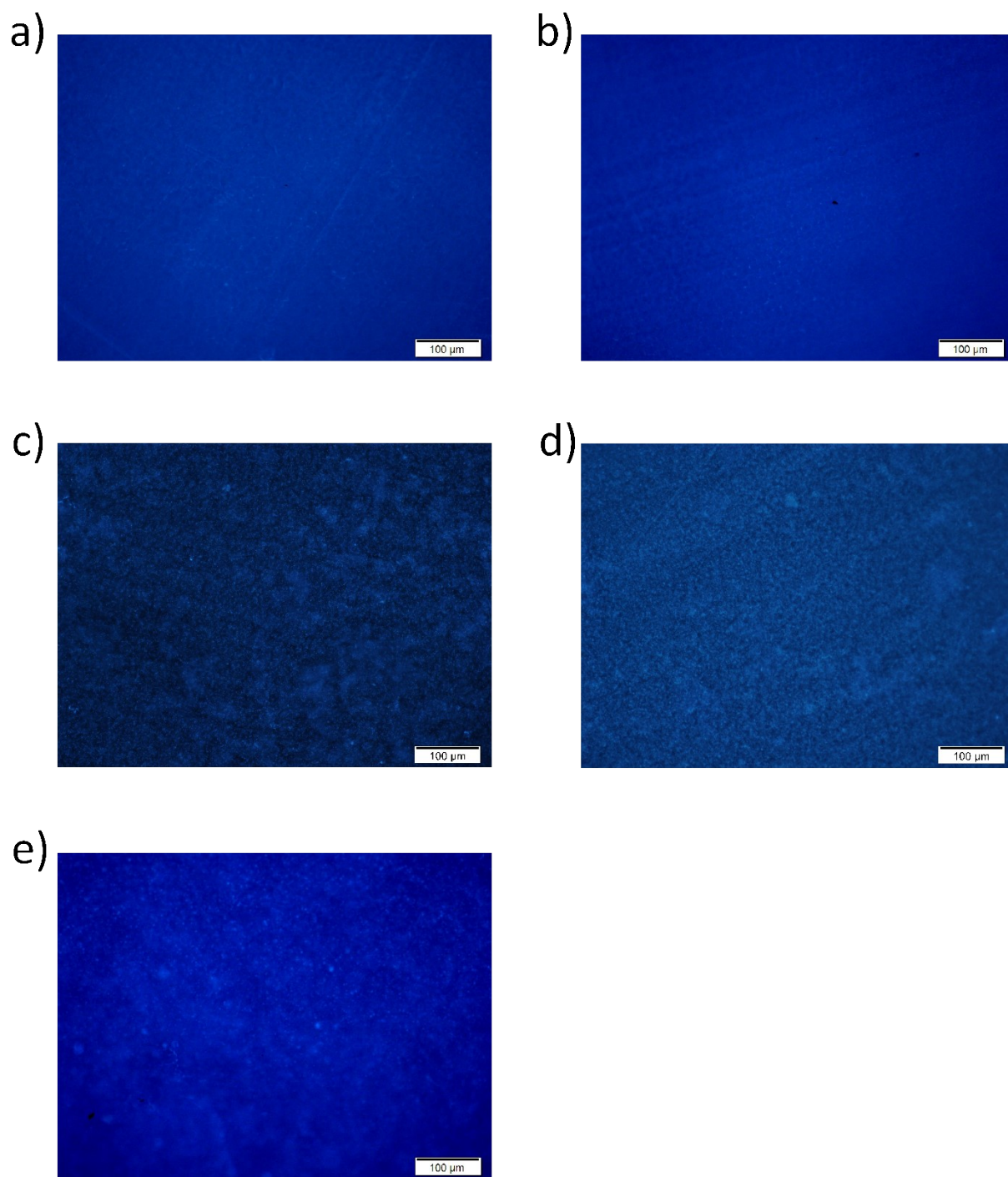


Figure S11. Fluorescence microscopy images of films of the following blends: a) PI/Py-PEB₅; b) PI/Py-PEB₁₀; c) PU/Py-PEB_{0.2}; d) PU/Py-PEB₁; e) PCL/Py-PEB₁. Droplet formation is clearly visible in c) d) and e), but less so in a) and b). Images were recorded with a wideband UV filter ($\lambda_{\text{ex}} = 330\text{-}385\text{ nm}$; $\lambda_{\text{em}} = 420\text{-}900\text{ nm}$, Olympus U-MWU2).

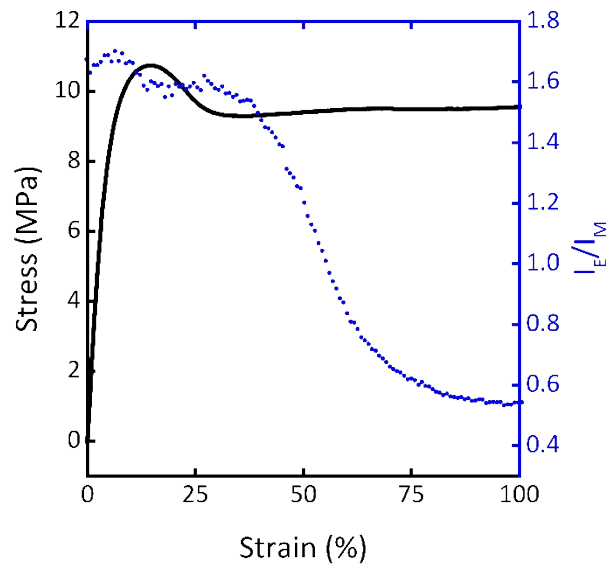


Figure S12. Magnification of the low-strain regime (0-100%) of the data shown in **Figure 3c**.

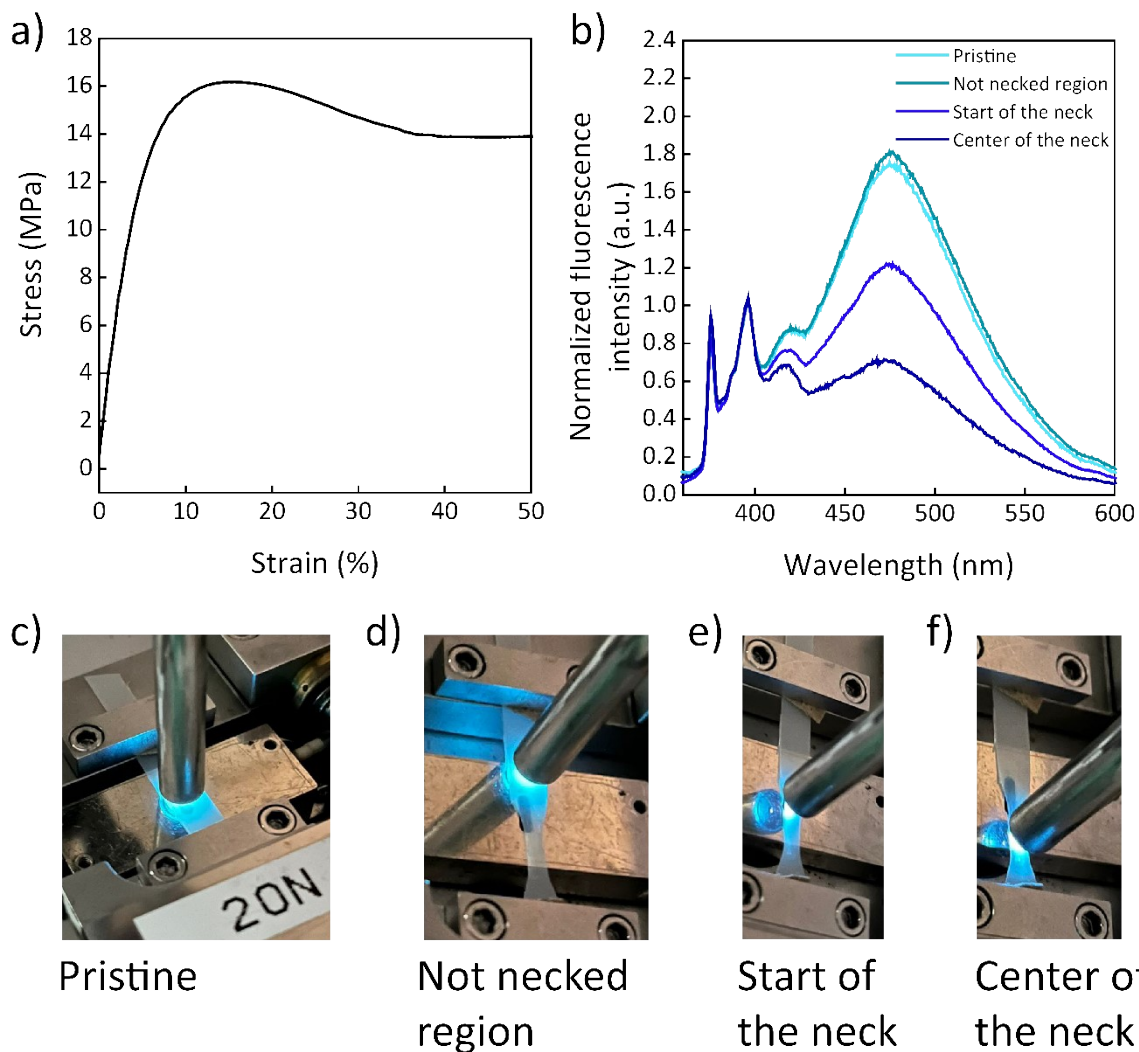


Figure S13. Possible scenarios of in-situ photoluminescence measurements during the stress-strain test of a polymer film that shows necking. a) Stress-strain curve of a PCL/Py-PEB₁ film. b) Fluorescence spectra of the pristine film and of the deformed film (50% strain) recorded in different locations of the sample. The four different spectra were acquired in the regions shown in pictures c)-f).

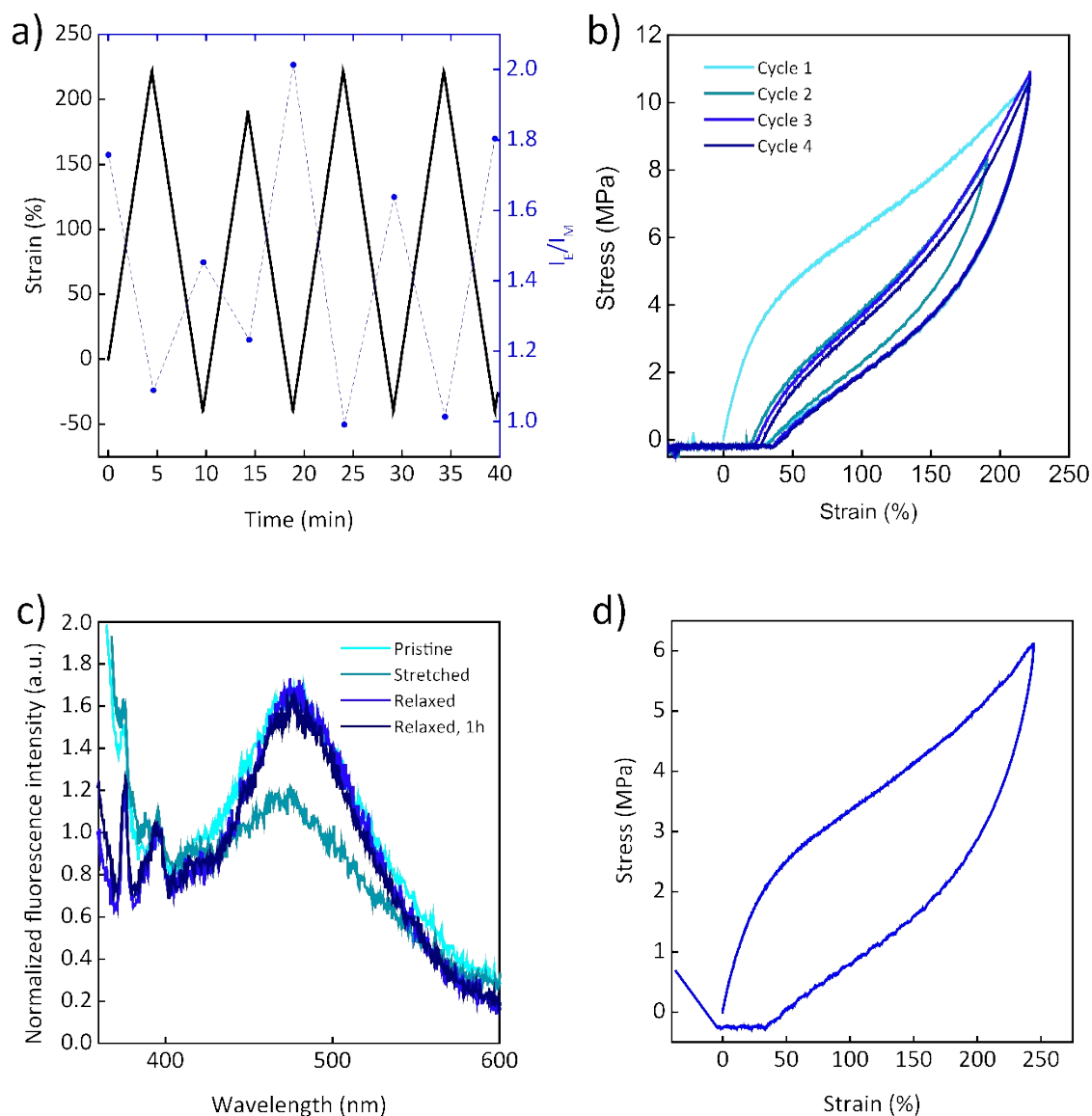


Figure S14. a) Cyclic deformation experiment of a PU/Py-PEB_{0.2} film. The sample was stretched and relaxed at a strain rate of ca. 50% min⁻¹. Fluorescence spectra were recorded of the stretched and relaxed sample for each cycle. b) Stress-strain curves acquired during the cyclic deformation experiment shown in a). c) Photoluminescence spectra of a PU/Py-PEB_{0.2} film that was stretched once, relaxed, and measured again 1 h after relaxation. d) Stress-strain curve relative to the stretching of the sample in c).