

Supporting information for the manuscript “Blending or bonding? Mechanochromism of an aggregachromic mechanophore in a thermoplastic elastomer”

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1. Conversion of AMP-Cl to AMP



Figure S1. AMP-Cl before (left) and after (right) the addition of NH_4Cl .

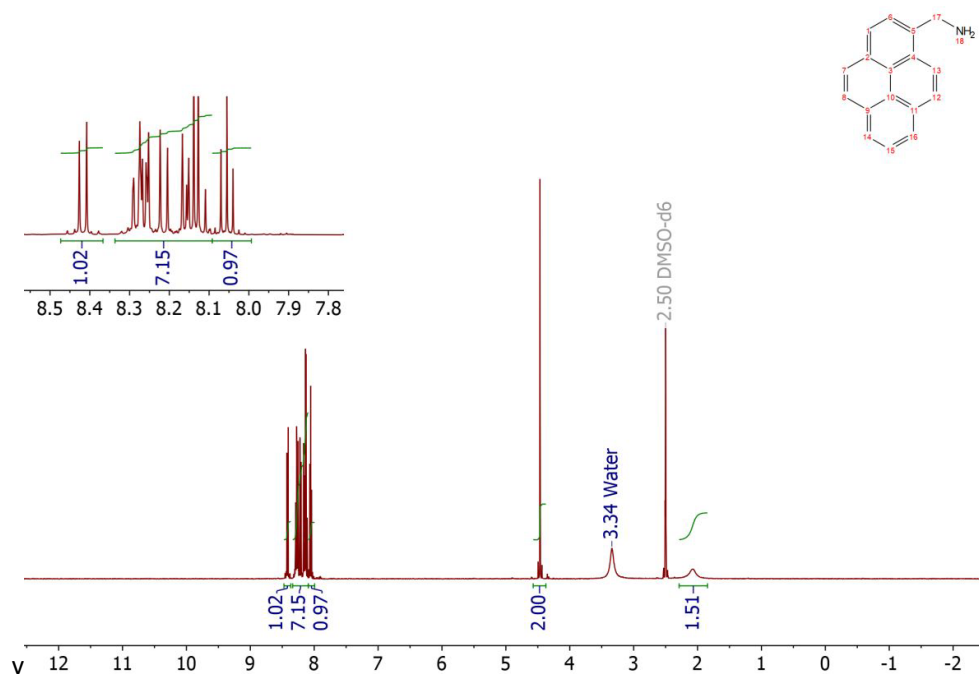


Figure S2. ¹H-NMR (500 MHz, DMSO-d₆, 25°C) of AMP.

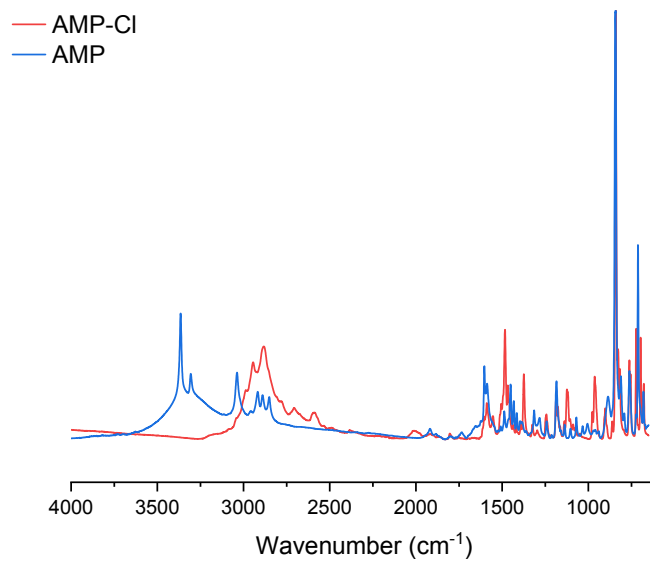


Figure S3. IR spectra of AMP-Cl (red) and AMP (blue).

2. Thermal treatment under vacuum of SEBS-MAH

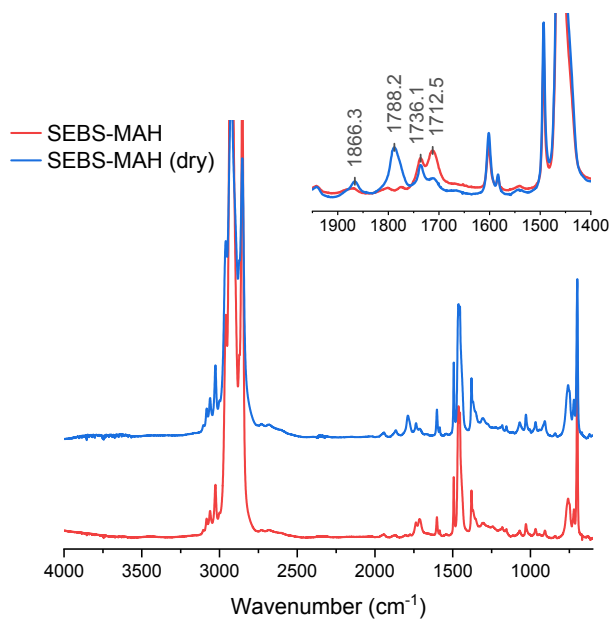


Figure S4. IR spectra of SEBS-MAH before (red) and after (blue) dried under vacuum to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydrides.

3. Functionalization of SEBS-MAH

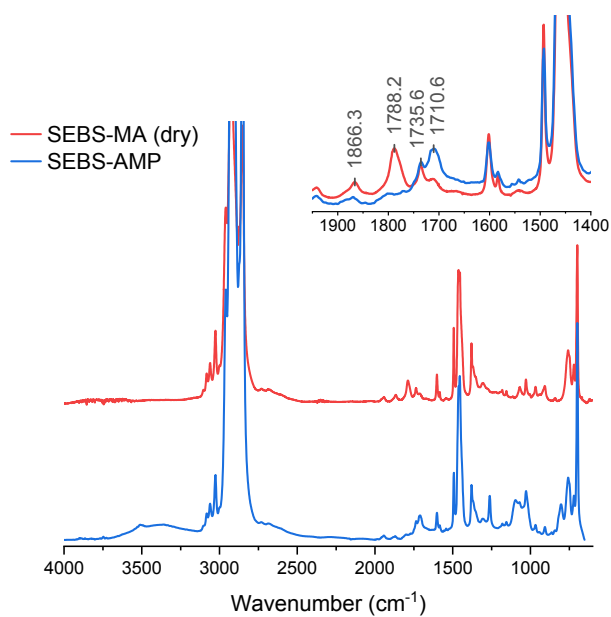


Figure S5. IR spectra of starting polymer matrix (SEBS-MAH, red) and after functionalization (SEBS-AMP, blue).

4. UV-Vis analysis to determine grafted pyrene

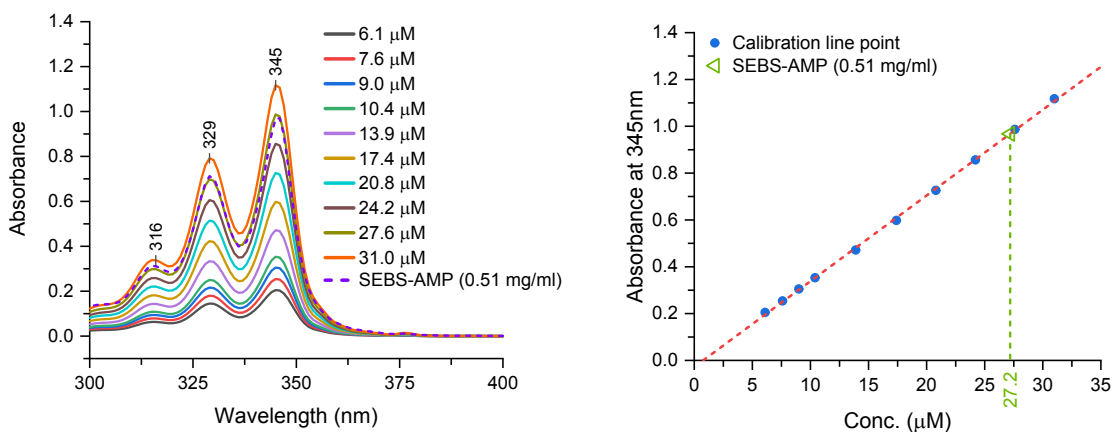


Figure S6. (a) UV-Vis spectra of AMP at different concentrations in toluene (line), and SEBS-AMP dissolved in toluene (dash); (b) calibration line and data for SEBS-AMP.

5. UV-Vis analysis of polymeric films

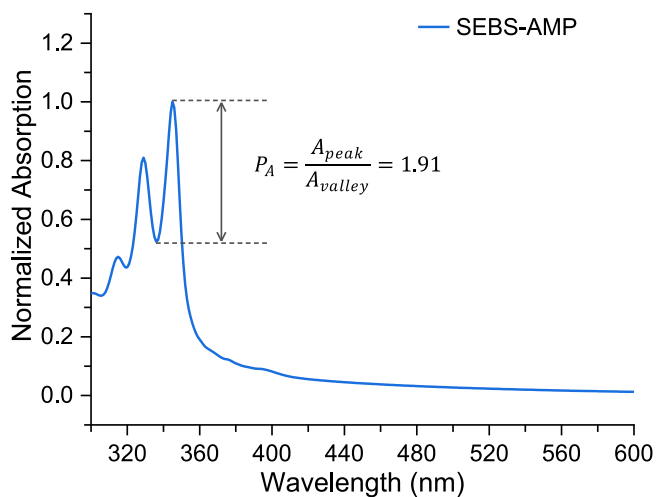


Figure S7. UV-Vis spectra of polymeric SEBS-AMP film. P_A represents the peak-to-valley ratio for the (0,0) transition, and A_{peak} and A_{valley} are the absorption intensity of the most intense band and the adjacent minimum at shorter wavelengths respectively [F. M. Winnik, Chem. Rev. **93**, 587-414 (1993)].

6. Thermal and mechanical analysis

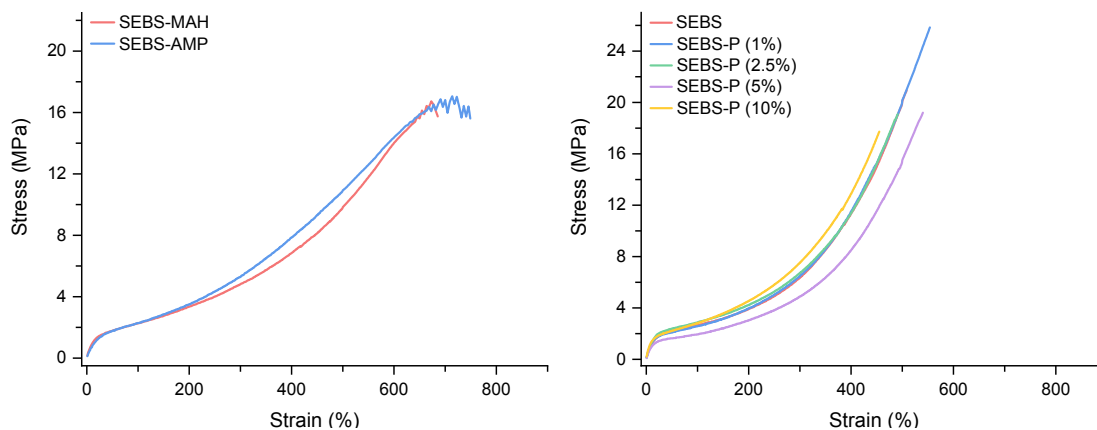


Figure S8. Stress-strain curves for covalently functionalized, blend samples and pristine polymers.

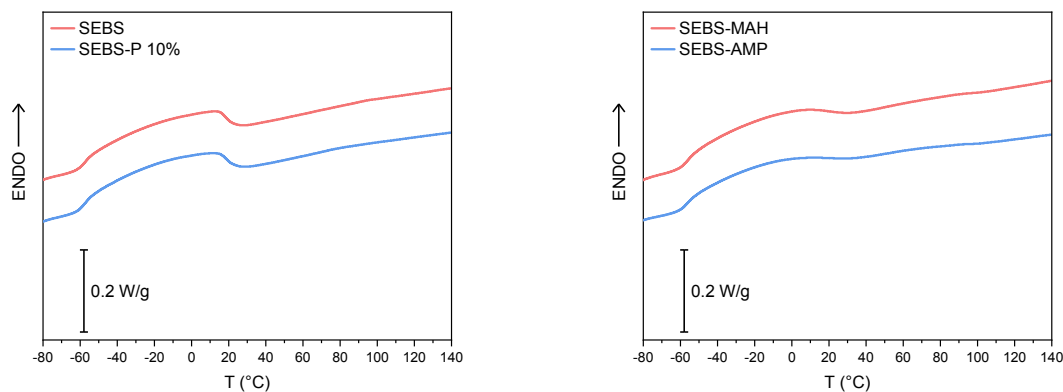


Figure S9. DSC curves for SEBS-P 10%, SEBS-AMP and pristine polymers (second heating scan).

Table S1. Thermal parameters (T_m : melting temperature of aliphatic block, T_g : glass transition temperature of aliphatic block, ΔH_m : melting enthalpy) for SEBS-P 10%, SEBS-AMP, and pristine polymers, determined in the second heating scan.

	T_m (°C)	T_g (°C)	ΔH_m (J/g)
SEBS	14.4	-57.0	13.2
SEBS-P 10%	14.6	-57.3	12.7
SEBS-MAH	7.2	-55.8	8.5
SEBS-AMP	4.2	-55.8	7.1

7. Mechanochromic systems

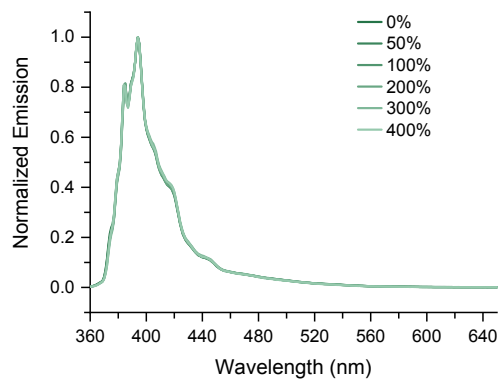


Figure S10. Normalized emission (λ_{exc} : 345 nm) for SEBS-P 1% at different stress.

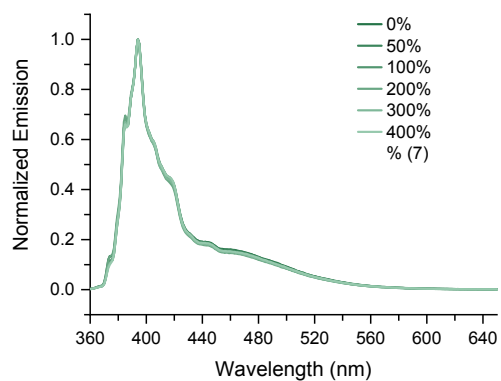


Figure S11. Normalized emission (λ_{exc} : 345 nm) for SEBS-P 2.5% at different stress.

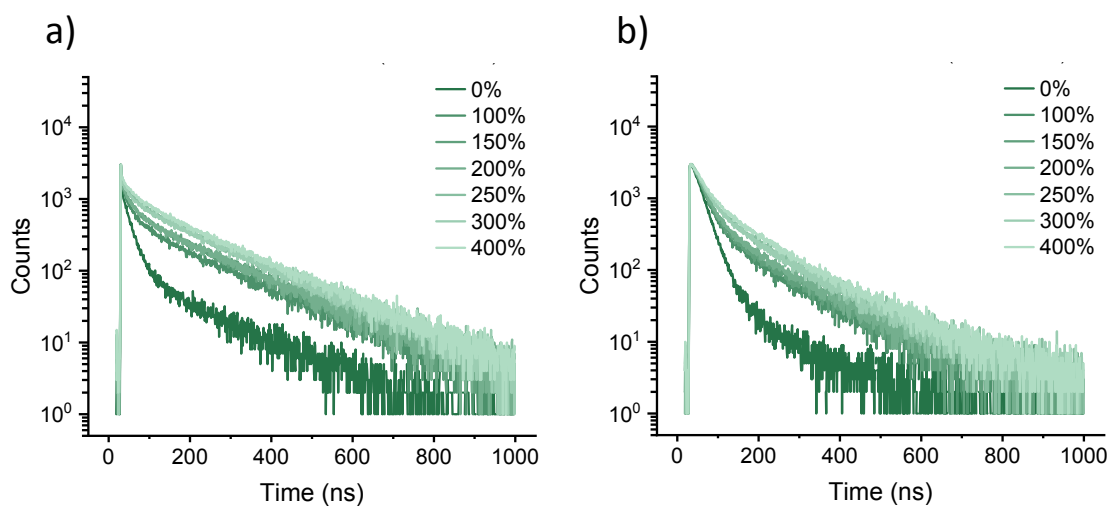


Figure S12. Emission decays of monomer ($\lambda_{em} = 398$ nm, a) and excimer ($\lambda_{em} = 470$ nm), b) emission in SEBS-P 10% at different stress.

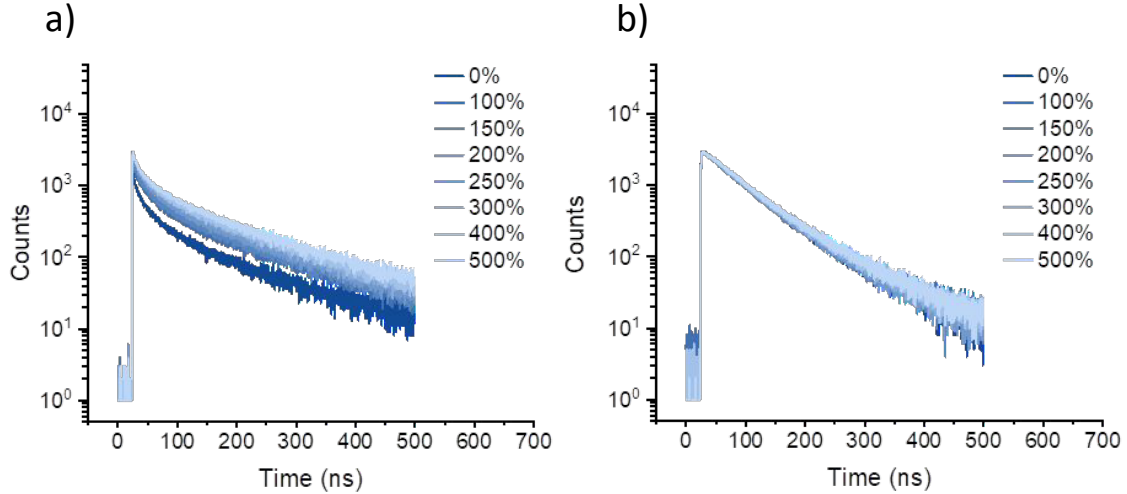


Figure S13. Emission decays of monomer ($\lambda_{em} = 398 \text{ nm}$, a) and excimer ($\lambda_{em} = 470 \text{ nm}$), b) emission in SEBS-AMP at different stress.

8. SNOM

The Scanning Near-field Optical Microscope (SNOM) setup is custom-built according to the configuration described in [P.G. Gucciardi, et al., “Versatile scanning near-field optical microscope for material science applications”, Rev. Sci. Instrum. **68**, 3088 (1997)], as sketched in Figure S14. The adopted probe is a tapered single-mode optical fiber featuring an apical aperture of 50 nm (nominal); the shear-force method is employed to monitor the probe-to-sample distance and keep it within the near-field range.

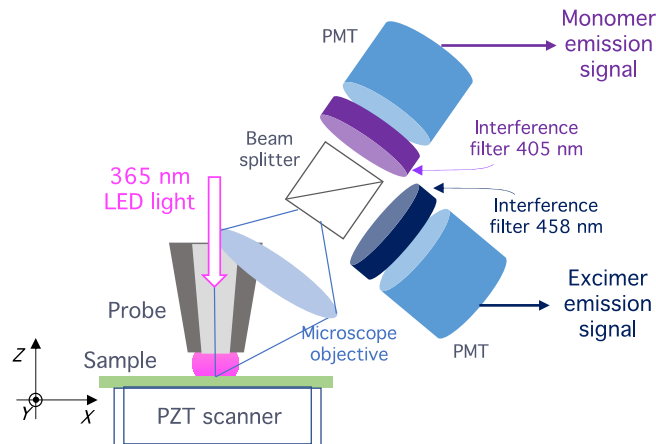


Figure S14. Simplified sketch of the SNOM setup: two distinct miniaturized photomultipliers (PMT) collect emission of the monomer and excimer bands. The sample is held by a piezoelectric (PZT) scanner of the hollow-tube kind, enabling sub-nm controlled displacements along the three (X , Y , Z) directions.

Operation in the near-field is assessed by the consistent increase of the collected signal during the probe-to-sample approach (Figure S15a), demonstrating its effective coupling with the material. Sub-wavelength lateral resolution is achieved in the actual conditions of the experiment: both maps acquired during the forward and backward directions of the SNOM raster scan show features with minimum size below 200 nm (Figure S15b).

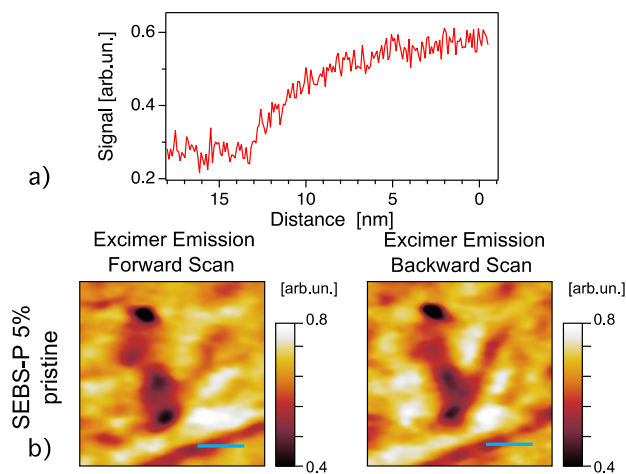


Figure S15. Emission signal as a function of the probe-to-sample distance acquired during an approach a); emission maps collected during the forward and backward directions of the SNOM raster scan b). Markers size is 400 nm; relative variations of the signal in forward and backward scans are typically within $\pm 10\%$. Data shown in the examples refer to the excimer emission from SEBS-P 5% in pristine conditions.

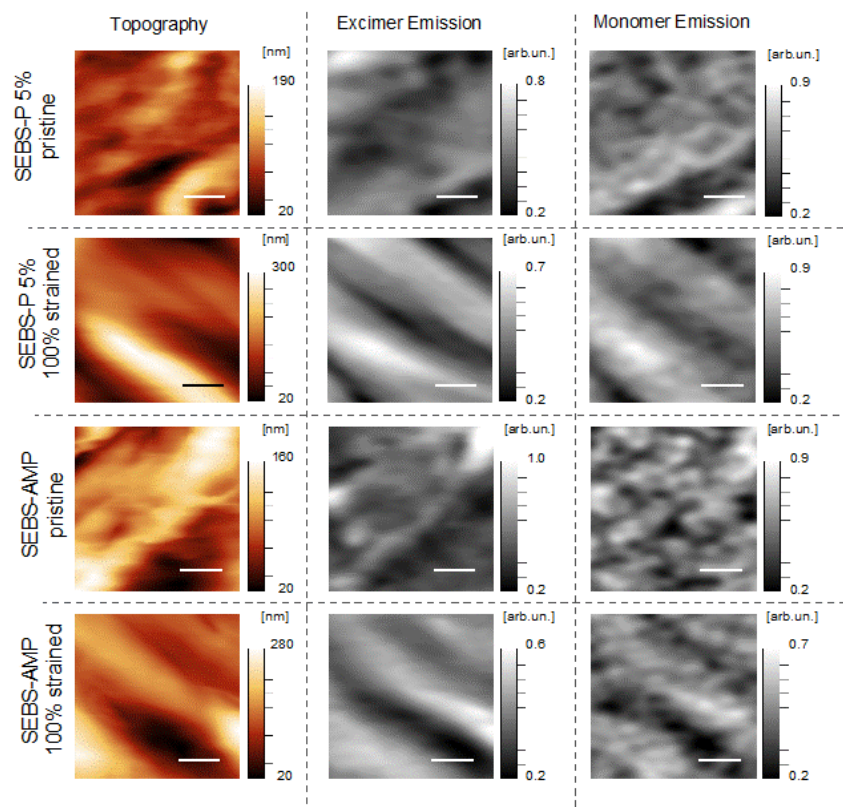


Figure S16. Topography and emission maps for SEBS-P 5% and SEBS-AMP samples, both in pristine and strained conditions. Marker size is 1 μm ; $\lambda_{exc} = 365 \text{ nm}$.

Emission domains are identified in the SNOM maps by using a cell-counting algorithm based on the Otsu method [N. Otsu, “A threshold selection method from gray-level histograms”, IEEE Trans. Sys. Man. Cyber. **9**, 62-66 (1979)] implemented in the Gwyddion 2.61 software [D. Nečas, et al., Cent. Eur. J. Phys. **10**, 181-

188 (2012)]. The algorithm sets a threshold in an intensity map, enabling separation in two distinct classes; threshold is determined via maximization of the intensity variance pertaining to each class. Figure S16 shows examples of the algorithm output. In the experiment, the approach has been applied to the whole set of available emission maps, leading to the domain average area and the relevant standard deviation plotted in Figure 5a of main text.

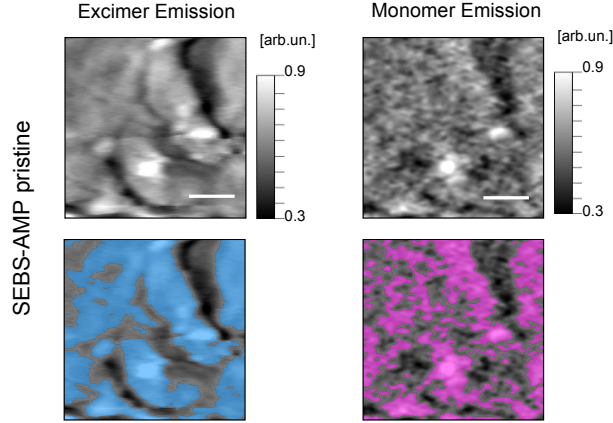


Figure S17. Examples of the Otsu algorithm applied to the SEBS-AMP film in pristine conditions (excimer emission): in the bottom line, the obtained emission domains are superposed to maps. Marker size is $2 \mu\text{m}$.

Cross-correlation analysis is used to determine the spatial interdependence between excimer and monomer emission. To this aim, individual maps simultaneously acquired during the same sample scan are first normalized to their dynamic range, according to

$$e'_{i,j} = 2 \frac{e_{i,j} - e_{avg}}{e_{max} - e_{min}} \quad (\text{S1})$$

$$m'_{i,j} = 2 \frac{m_{i,j} - m_{avg}}{m_{max} - m_{min}} \quad (\text{S2})$$

where $e_{i,j}$ and $m_{i,j}$ are the excimer and monomer emission signals detected at the i,j point of the map, e_{max} , m_{max} the maximum, e_{min} , m_{min} the minimum, and e_{avg} , m_{avg} the average signals detected in the corresponding maps. The so-determined normalized signals $e'_{i,j}$ and $m'_{i,j}$, ranging from -1 to +1, are then used to build a cross-correlation map, whose elements $c_{i,j}$ are calculated as

$$c_{i,j} = \sum_{k=0}^{N-1} \sum_{\ell=0}^{N-1} e'_{i+k,j+\ell} m'_{k,\ell} \quad (\text{S3})$$

where summations extend over the whole map, N being the number of points in every line and column of the square map (N is typically equal to 256). The cross-correlation map C_{em} showing $c_{i,j}$ values can finally be drawn. A simple Python code has been used for calculations.

The mean value of the cross-correlation term (C_{em}) was found lower for pristine and drawn SEBS-AMP compared to SEBS-P (Table S2). This is in agreement with the more efficient dispersion of PL domains in SEBS-AMP.

These results support the hypothesis that the stretching affects the distribution of the domains, in particular, increasing the cross-correlation between the distribution of pyrene in the monomeric and aggregated forms. This effect is particularly evident in the case of SEBS-AMP, which presented a more dispersed distribution in the pristine state.

Table S2. The mean value of the cross-correlation term (C_{em}) for SEBS-P 10% and SEBS-AMP at 0% and 100% of strain.

	C_{em}	
	pristine	drawn
SEBS-P 10%	0.83±0.11	0.88±0.10
SEBS-AMP	0.60±0.16	0.75±0.14