Comparative mechanochromic performance of perylene diimide-doped polyurethanes: blending vs bonding

Supporting Information

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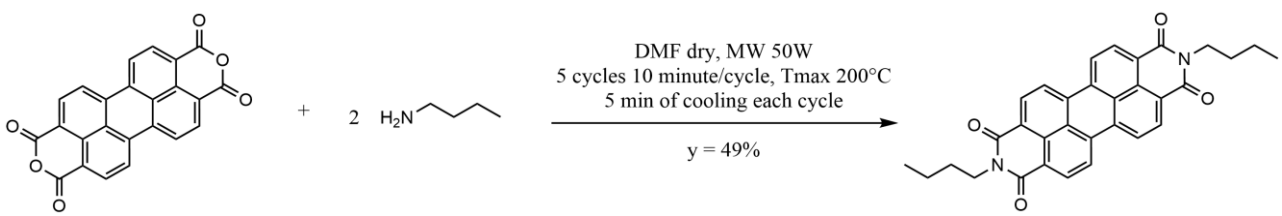
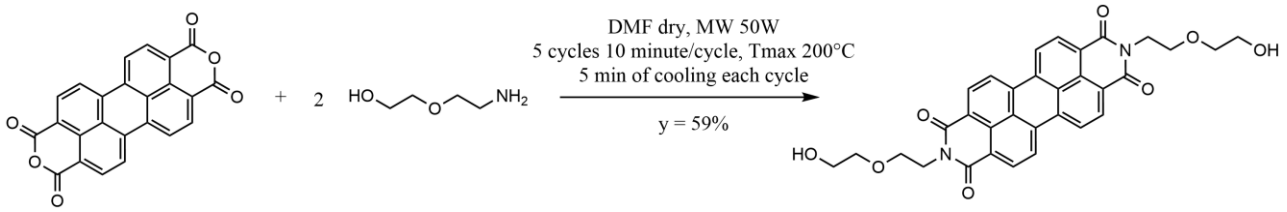
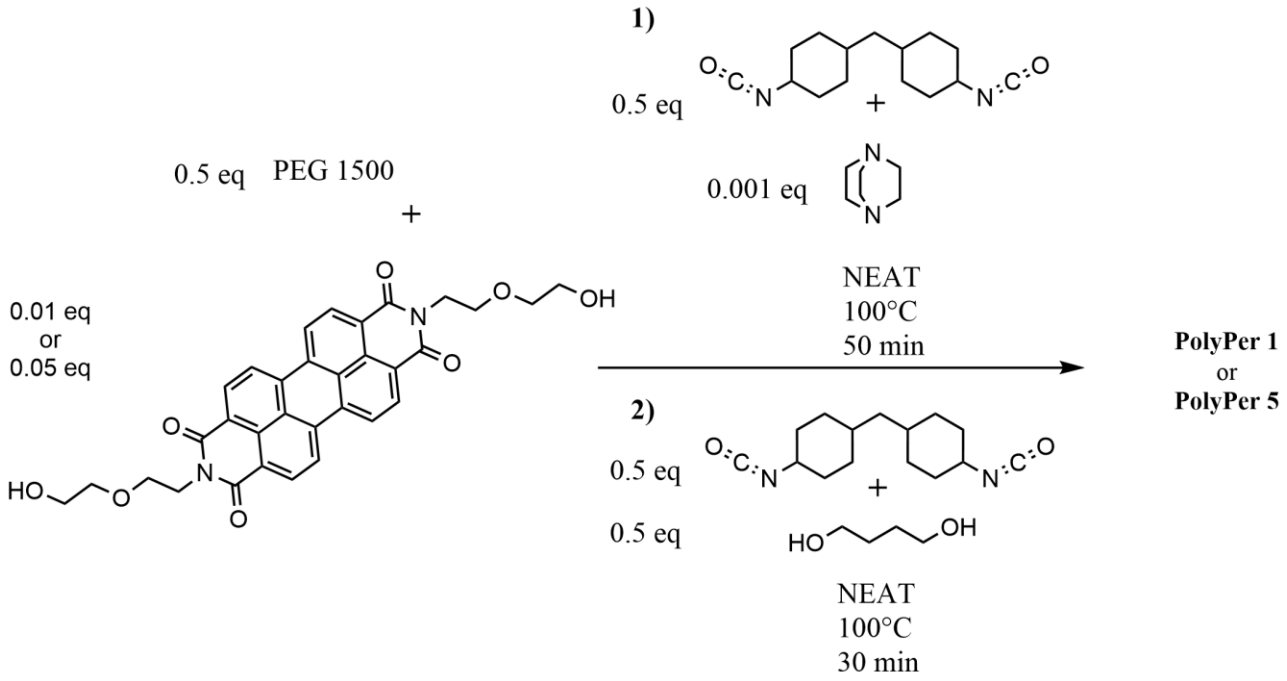
1. Synthetic Schemes



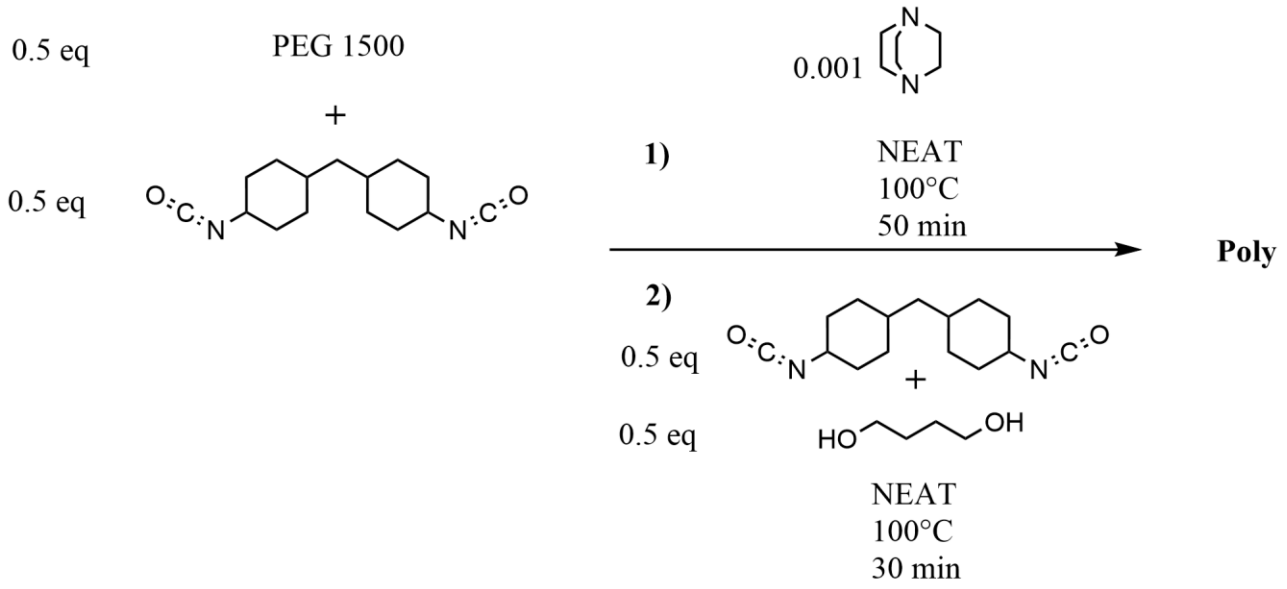
Scheme S1. Synthesis of Per.



Scheme S2. Synthesis of Per-OH.



Scheme S3. Synthesis of PolyPer1 and PolyPer5.



Scheme S4. Synthesis of Poly.

2. NMR

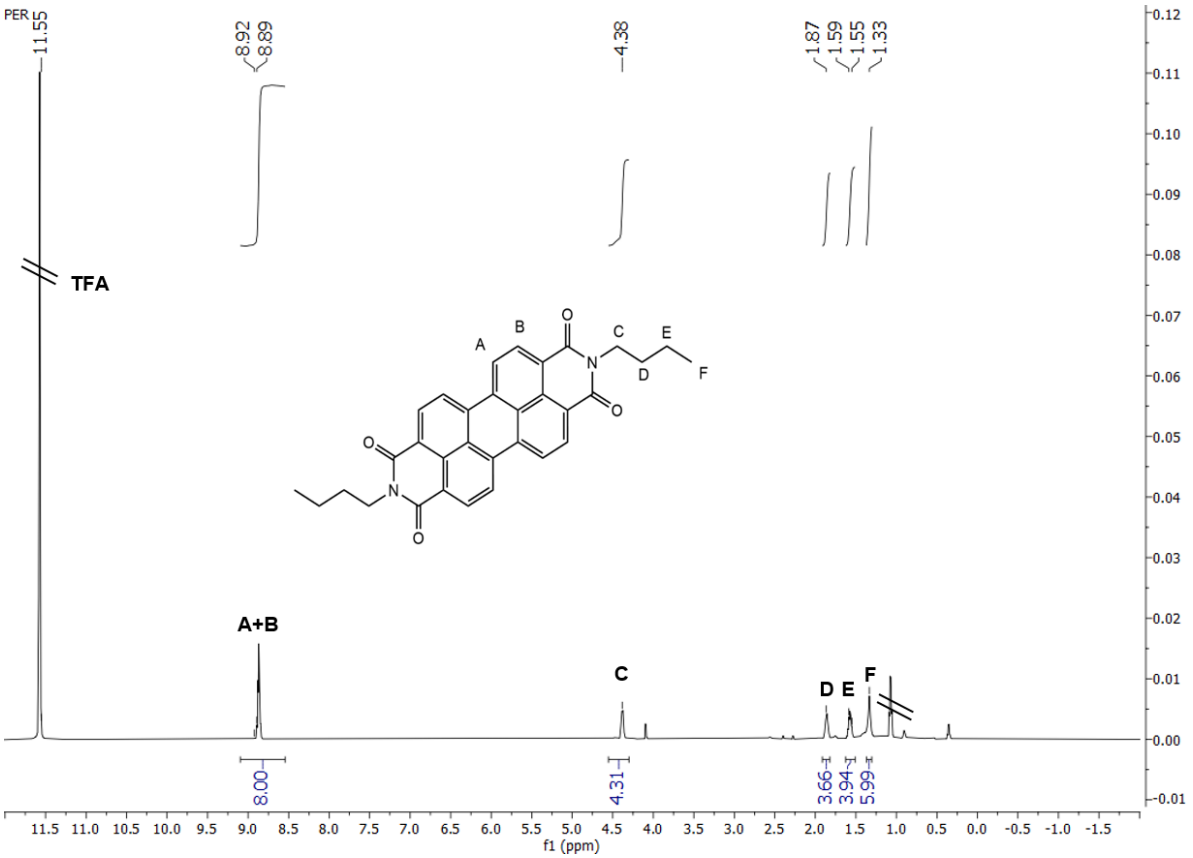


Figure S1. ^{1}H NMR of Per (deuterated TFA, 600 MHz, 298 K).

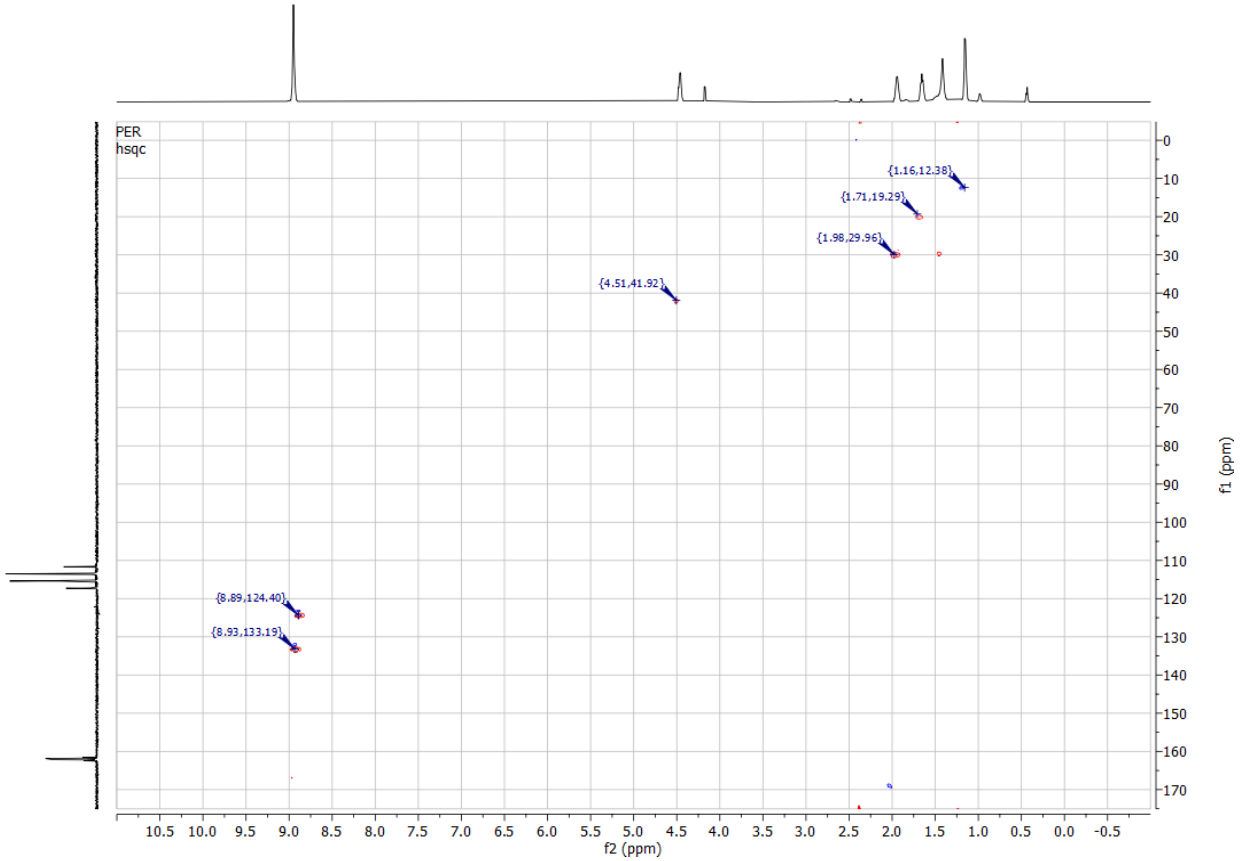


Figure S2. HSQC of Per (deuterated TFA, 151 MHz, 298 K).

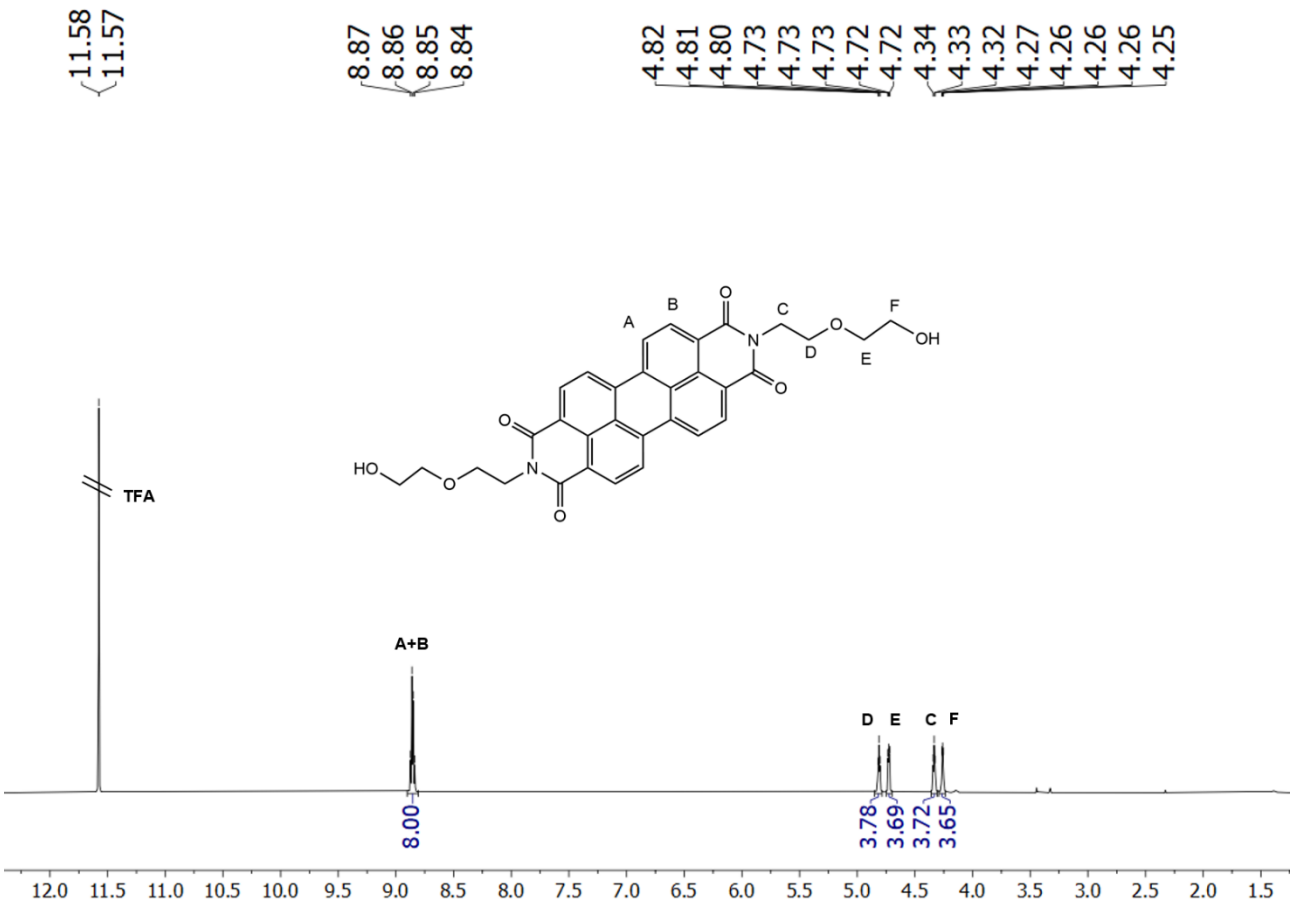


Figure S3. ^{1}H NMR of Per-OH (deuterated TFA, 600 MHz, 298 K).

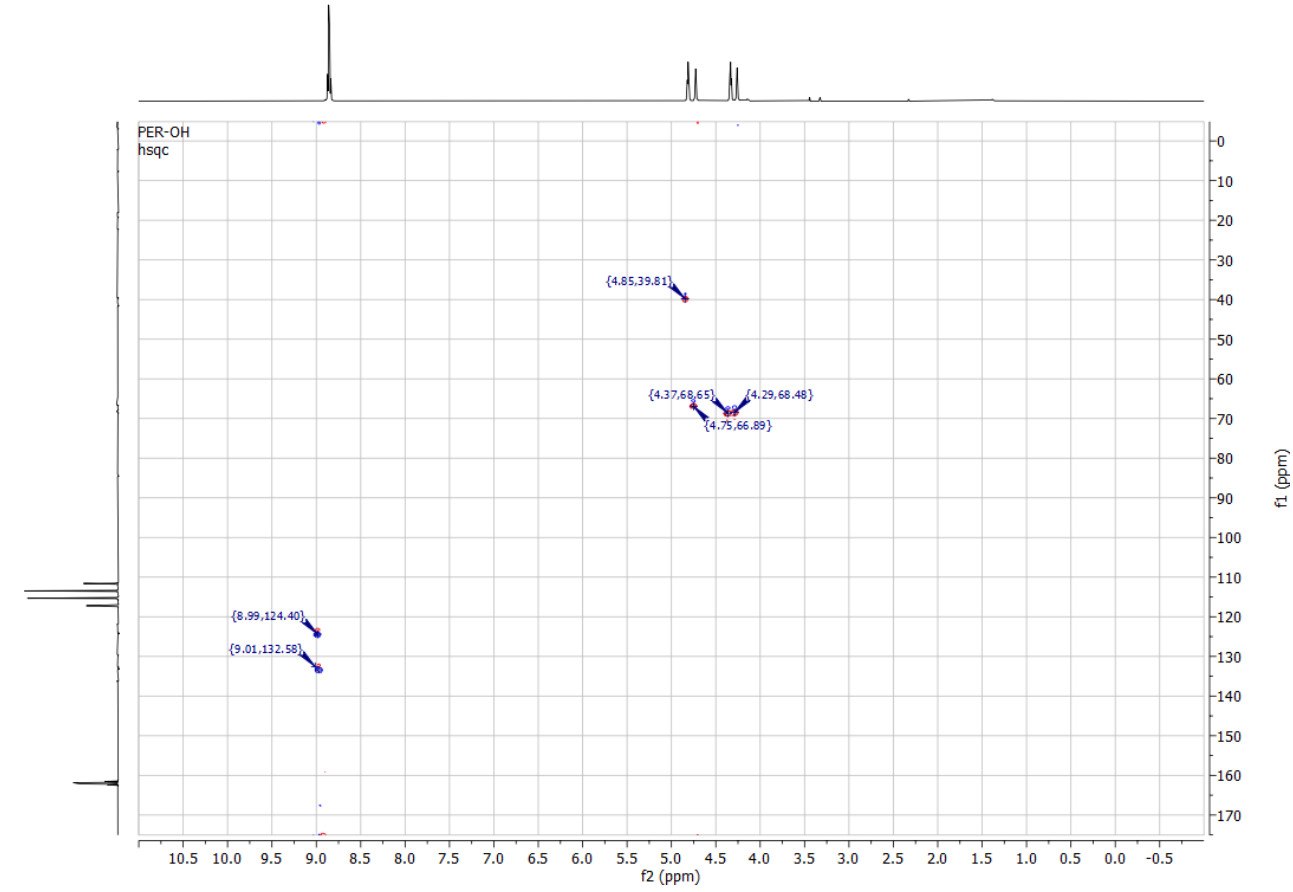


Figure S4. HSQC of Per-OH (deuterated TFA, 151 MHz, 298 K).

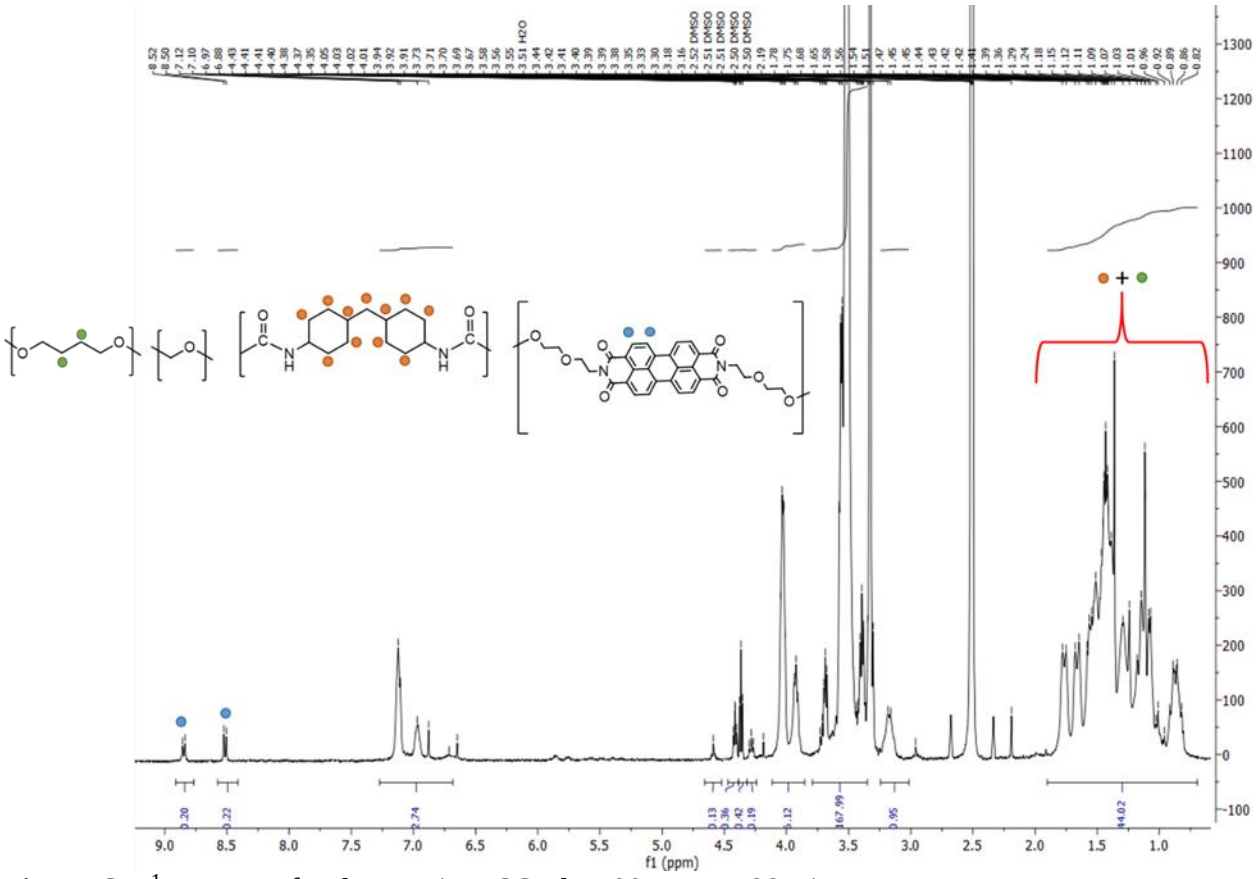


Figure S5. ^{1}H NMR of PolyPer5 (DMSO_d$_6$, 400 MHz, 298 K).

3. Gel Permeation Chromatography

Table S1. GPC data of TPU, Poly, PolyPer1 and PolyPer5: number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (Đ).

Sample	**M_n [g mol^{-1}]**	**M_w [g mol^{-1}]**	**Đ**
TPU	93410	310570	3.3
PEG1500	660	870	1.3
Poly	1960	3630	1.9
PolyPer1	1960	3360	1.7
PolyPer5	2300	4640	2.0

4. Calorimetric data of bulk PU and Films

Table S2. Calorimetric data of bulk PU and films.

Sample	T_g [°C]	ΔC_p [J·g^{-1}·°C^{-1}]	T_m [°C]	ΔH_m (PEG segments) [J·g^{-1}]
Poly[a]	-45	0.16	42	63.1
PolyPer1[a]	-46	0.18	36	52.6
PolyPer5[a]	-46	0.11	32	40.1
D-0.15[b]	-45	0.37	44	12.2
D-0.78[b]	-46	0.23	41	15.6
MC-0.15[b]	-44	0.36	40	11.8
MC-0.78[b]	-43	0.39	42	8.3

a) Calorimetric data are referred to the heating scan after controlled cooling at 10 °C min^{-1}.

b) Calorimetric data are referred to the first heating scan.

5. DSC and calorimetric data of TPU

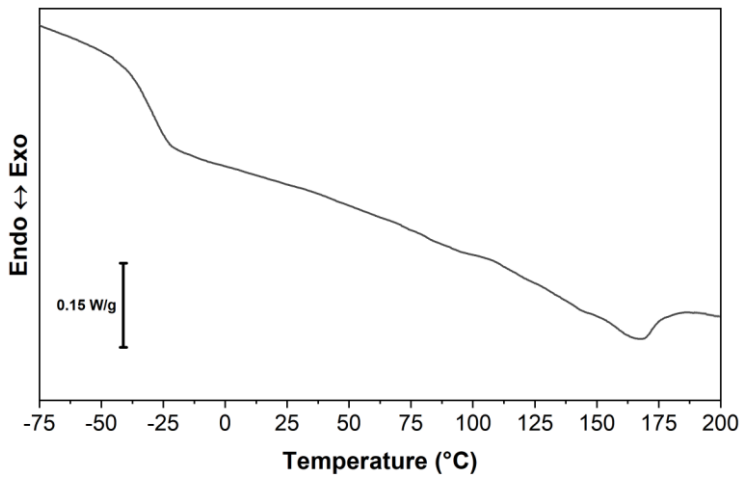


Figure S6. DSC scans after controlled cooling at 10 °C min^{-1} of TPU.

Table S3. Calorimetric data are referred to the heating scan after controlled cooling at 10 °C min^{-1}.

Sample	T_g [°C]	ΔC_p [$J \cdot g^{-1} \cdot °C^{-1}$]	T_m [°C]	ΔH_m [$J \cdot g^{-1}$]
TPU	-30	0.41	164	13.4

6. DMTA analysis

DMTA analysis was carried out to shed light on the miscibility between **Poly** and **TPU**. The pristine materials display a single loss modulus peak (as well as a single tanδ peak) ascribable to the glass transition, located at -52 °C for **Poly** and at -32 °C for **TPU**. Likewise, the analyzed blend (**MC-0.15**) shows a single peak of loss modulus at the intermediate temperature of -45°C. Therefore, in the blend, the TPU and the synthetized PU form a single miscible amorphous phase.

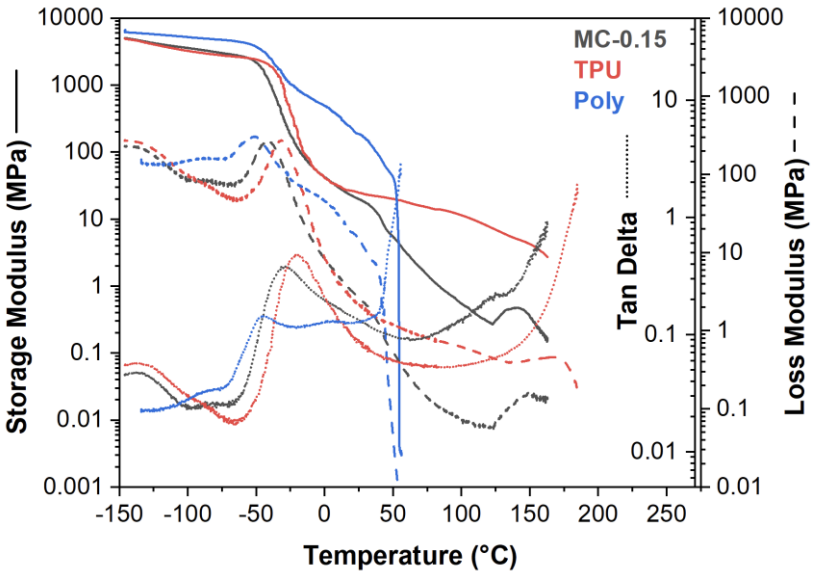


Figure S7. DMTA analysis of **MC-0.15** (black), **TPU** (red), and **Poly** (blue). Storage modulus (solid line), loss modulus (dashed line) and tanδ (dotted line) are reported.

7. Mechanical data and pictures under UV light of D and MC samples

Table S4. Mechanical data of **D** and **MC** samples.

Sample	Stress at break [MPa]	Strain at break [%]	Young's Modulus [MPa]
D-0.15	20 ± 3	$1.32 \cdot 10^3 \pm 0.05 \cdot 10^3$	5.3 ± 0,4
D-0.78	17 ± 4	$1.2 \cdot 10^3 \pm 0.1 \cdot 10^3$	6.0 ± 0,3
MC-0.15	19 ± 4	$1.2 \cdot 10^3 \pm 0.1 \cdot 10^3$	5.4 ± 0.4
MC-0.78	18 ± 6	$1.2 \cdot 10^3 \pm 0.1 \cdot 10^3$	6 ± 1

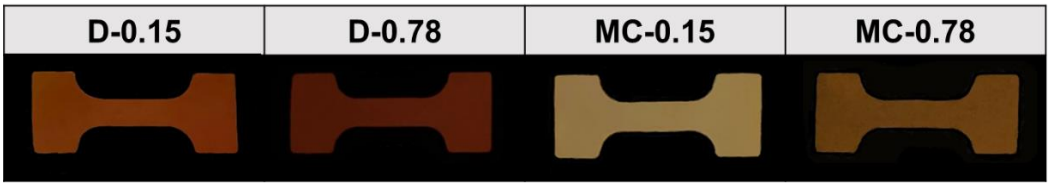


Figure S8. Images under UV light (λ_{ex}=365 nm) of films of **D** and **MC** samples.

8. Mechanochromic characterization

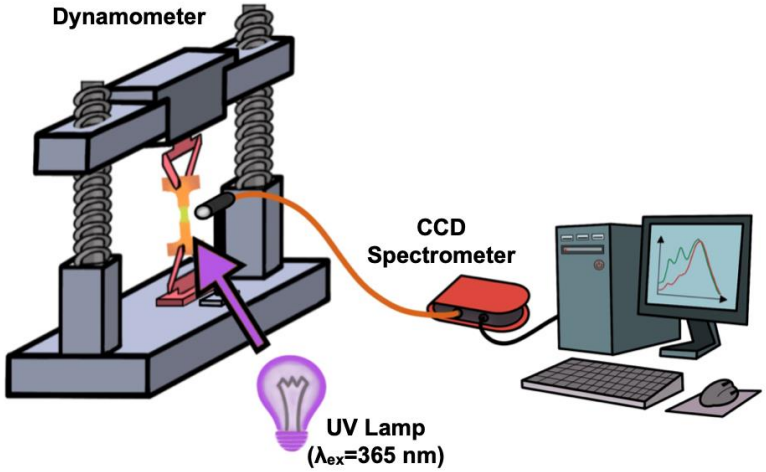


Figure S9. Schematic representation of the setup employed for the mechanochromic characterizations.

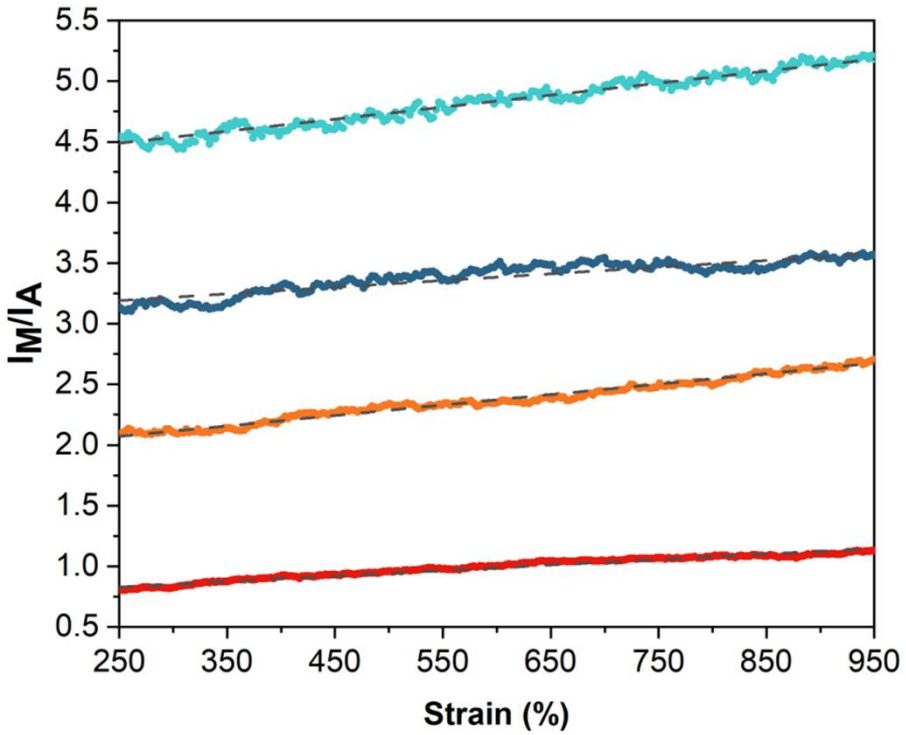


Figure S10. I_M/I_A (dots) plotted versus strain in the range 250% - 950%, fitted with a linear function (dashed line): D-0.15 (orange), D-0.78 (red), MC-0.15 (cyan,) and MC 0.78 (blue). The results reported are averaged among three samples.

Table S5. Results of the linear fit for D and MC samples.

Sample	Slope	R^2
D-0.15	$8.62 \cdot 10^{-4} \pm 0.07 \cdot 10^{-4}$	0.98
D-0.78	$4.55 \cdot 10^{-4} \pm 0.05 \cdot 10^{-4}$	0.97
MC-0.15	$9.9 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$	0.96
MC-0.78	$5.5 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$	0.86

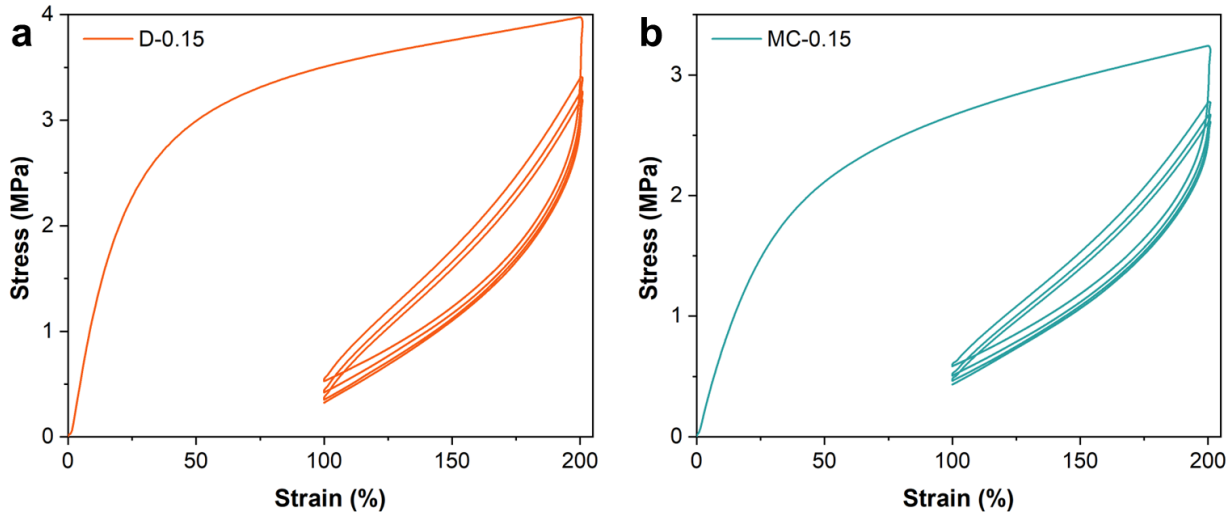


Figure S11. Stress-strain behavior of a) D-0.15 and b) MC-0.15 when deformed through multiple cycles. These stress-strain curves correspond to the loading-unloading cycles reported in Figure 6e and f as a function of time.

Table S6. Calorimetric and mechanochromic data before and after stress-relaxation experiments.

Sample	**Initial ΔH_m [J g^{-1}]**	**ΔH_m after relaxation [J g^{-1}]**	**Initial I_M/I_A**	**I_M/I_A max**	**I_M/I_A after relaxation**
D-0.15	12.2	16.0	1.216	1.44[a]	1.250
D-0.78	15.6	15.9	0.370	0.46[b]	0.336
MC-0.15	11.8	12.4	3.538	4.41[c]	3.294

a) at 135 s

b) at 130 s

c) at 130 s