

Electronic Supplementary Information

Spatio-temporal investigation of the crosslinking and the mechanical properties in a UV-curable rubber bearing photo-dimerizable moieties

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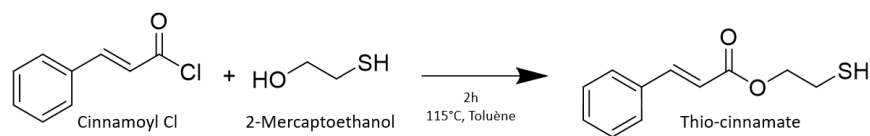
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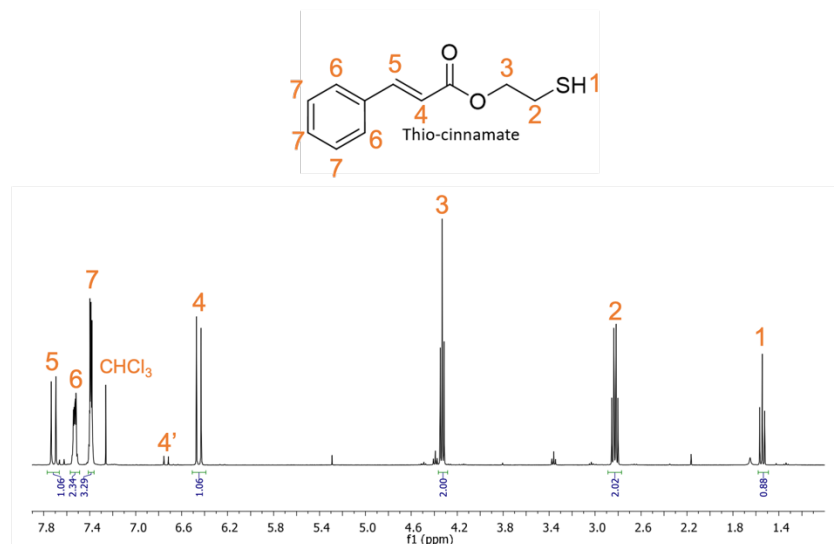
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I. Characterization of the thio-cinnamate ester, TC



Scheme S1: Synthesis pathway for the thio-cinnamate ester, TC



II. ^1H NMR characterization of TC-PBut for $X = 0.25$

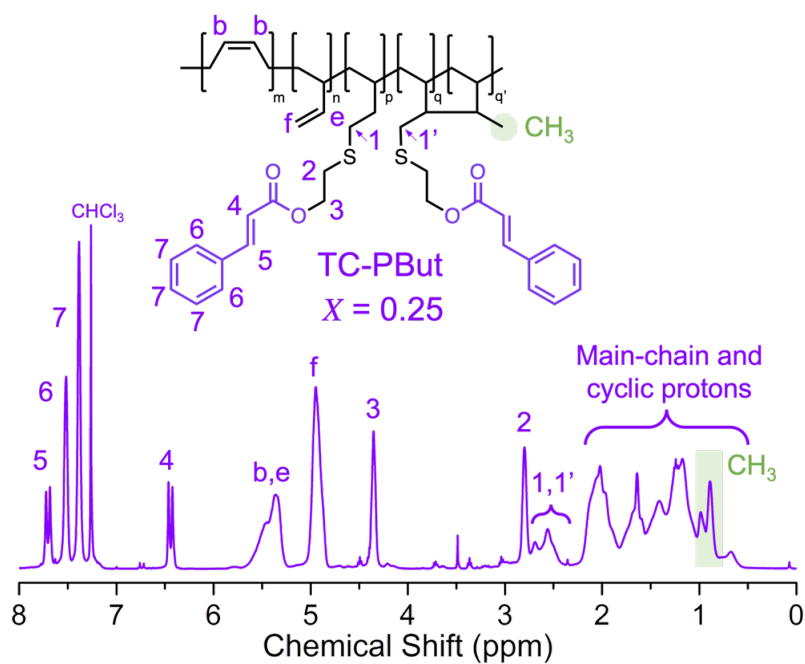


Figure S2: ^1H NMR spectrum of TC-PBut, $X = 0.25$ (400 MHz, CDCl_3)

III. Calculation of x_{funct} , x_{unreact} , and x_{cycle}

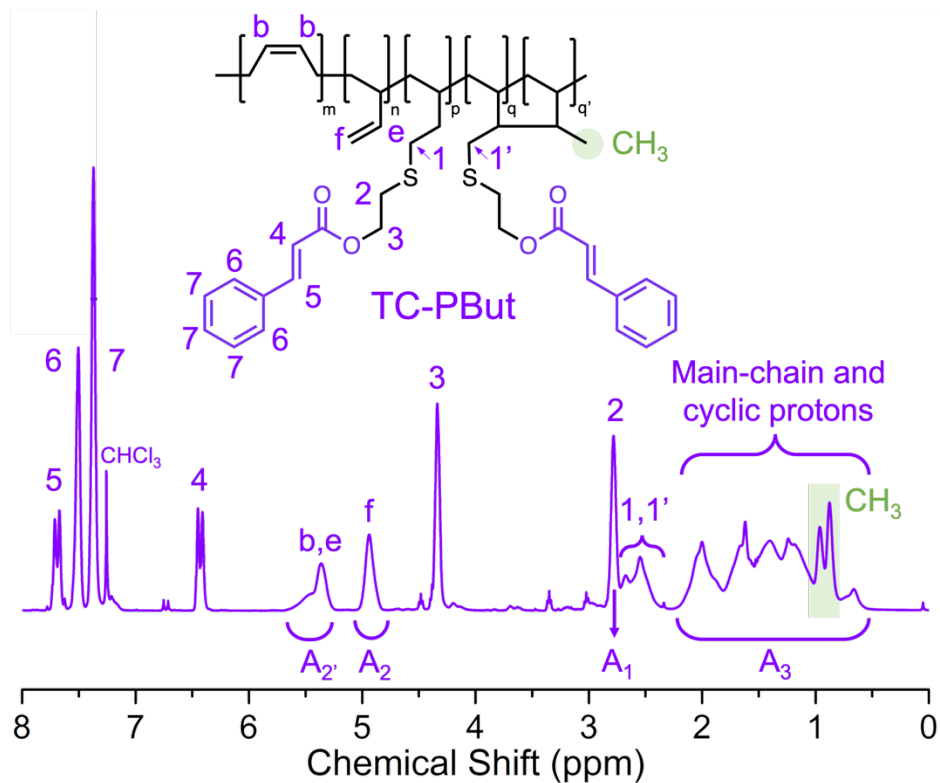


Figure S3: ^1H NMR spectrum of **TC-PBut**, $X = 0.5$ (400 MHz, CDCl_3)

It is possible to calculate x_{funct} , x_{unreact} , and x_{cycle} from the integrals, A_1 , A_2 , A_2' and A_3 from the RCH_2S - methylene protons (2), the $\text{H}_2\text{C}=\text{CH}$ - alkenic protons (f), the $-\text{HC}=\text{CH}-$ and $\text{H}_2\text{C}=\text{CH}$ - alkenic protons (b, e), and the aliphatic protons of chemical shifts below 2.2 ppm, respectively. In terms of the indices defined in **Figure S3**:

$$S1 \begin{cases} A_1 = 2p + 2q \\ A_2 = 2n \\ A_{2'} = 2m + n \\ A_3 = 4m + 3n + 5p + 4q + 7q' \\ q = q' \end{cases}$$

Moreover, the direct mathematical definitions of x_{funct} and x_{unreact} are given by:

$$S2 \begin{cases} x_{\text{funct}} = \frac{p + q}{m + n + p + q + q'} \\ x_{\text{unreact}} = \frac{m + n}{m + n + p + q + q'} \end{cases}$$

From the system of equations S1, we have:

$$S1 \begin{cases} p + q = A_1/2 \\ n = A_2/2 \\ m = A_{2'}/2 - A_2/4 \\ A_3 = 2A_{2'} - A_2 + 3A_2/2 + 5(p + q) + 6q \\ q = q' \end{cases}$$

$$\Leftrightarrow S1 \begin{cases} p + q = A_1/2 \\ n = A_2/2 \\ m = A_{2'}/2 - A_2/4 \\ A_3 = 2A_{2'} + A_2/2 + 5A_1/2 + 6q \\ q = q' \end{cases}$$

$$\Leftrightarrow S1 \begin{cases} p + q = A_1/2 \\ n = A_2/2 \\ m = A_{2'}/2 - A_2/4 \\ q = A_3/6 - A_{2'}/3 - A_2/12 - 5A_1/12 \\ q = q' \end{cases}$$

By reinjecting these equations in S2, it comes:

$$S2 \begin{cases} x_{funct} = \frac{A_1/2}{A_{2'}/2 - A_2/4 + A_2/2 + A_1/2 + A_3/6 - A_{2'}/3 - A_2/12 - 5A_1/12} \\ x_{unreact} = \frac{A_{2'}/2 - A_2/4 + A_2/2}{A_{2'}/2 - A_2/4 + A_2/2 + A_1/2 + A_3/6 - A_{2'}/3 - A_2/12 - 5A_1/12} \end{cases}$$

$$\Leftrightarrow S2 \begin{cases} x_{funct} = \frac{A_1/2}{A_1/12 + A_2/6 + A_{2'}/6 + A_3/6} \\ x_{unreact} = \frac{A_{2'}/2 + A_2/4}{A_1/12 + A_2/6 + A_{2'}/6 + A_3/6} \end{cases}$$

$$\Leftrightarrow S2 \begin{cases} x_{funct} = \frac{6A_1}{A_1 + 2A_2 + 2A_{2'} + 2A_3} \\ x_{unreact} = \frac{6A_{2'} + 3A_2}{A_1 + 2A_2 + 2A_{2'} + 2A_3} \end{cases}$$

And

$$x_{cycle} = 1 - x_{funct} - x_{unreact}$$

The following Table gather the values measured for the different integrals of the NMR spectra (the peak 3 was used as a reference), and the corresponding values of x_{funct} , $x_{unreact}$, and x_{cycle} , using the above equations:

X	A_1	A_2	$A_{2'}$	A_3	x_{funct} (%)	x_{unreact} (%)	x_{cycle} (%)
0.5	1.96	1.32	1.33	14.38	33.0	33.5	33.5
0.25	1.98	5.38	4.19	24.10	17.1	59.5	23.3

Table S1 : Integral values measured for the NMR spectra of TC-PBut, $X = 0.25$ and $X = 0.5$

IV. FTIR characterization of TC-PBut for $X = 0.25$

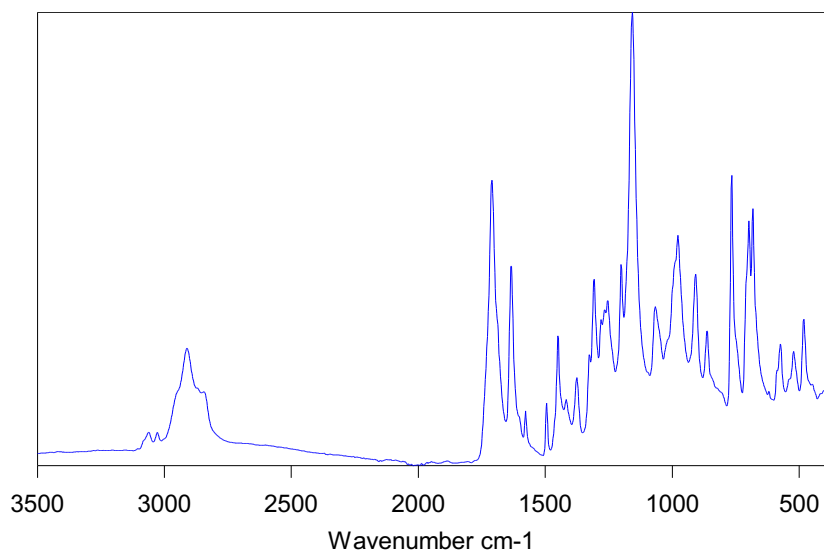


Figure S4: FTIR spectrum of TC-PBut, $X = 0.25$

V. Size Exclusion Chromatography analysis of PBut, and TC-PBut for $X = 0.25$ and 0.50

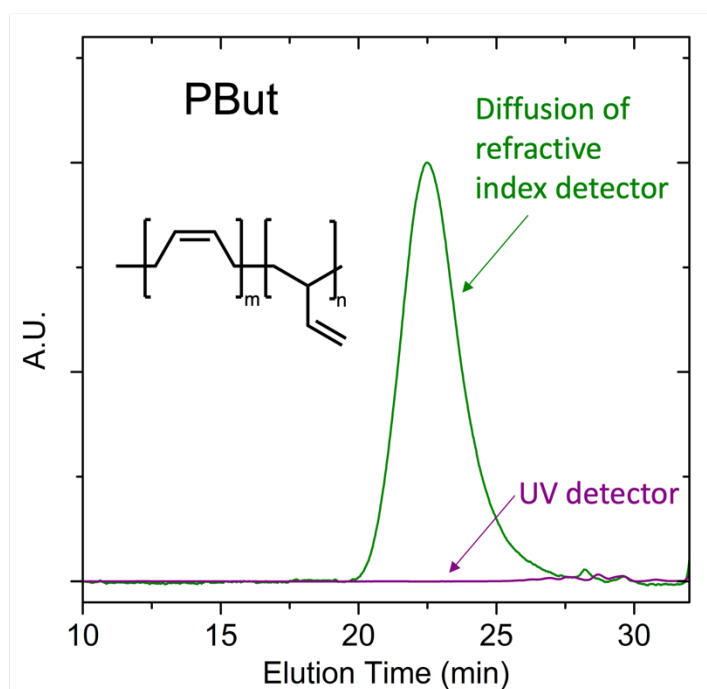


Figure S5: SEC elugram of PBut (THF, polystyrene calibration)

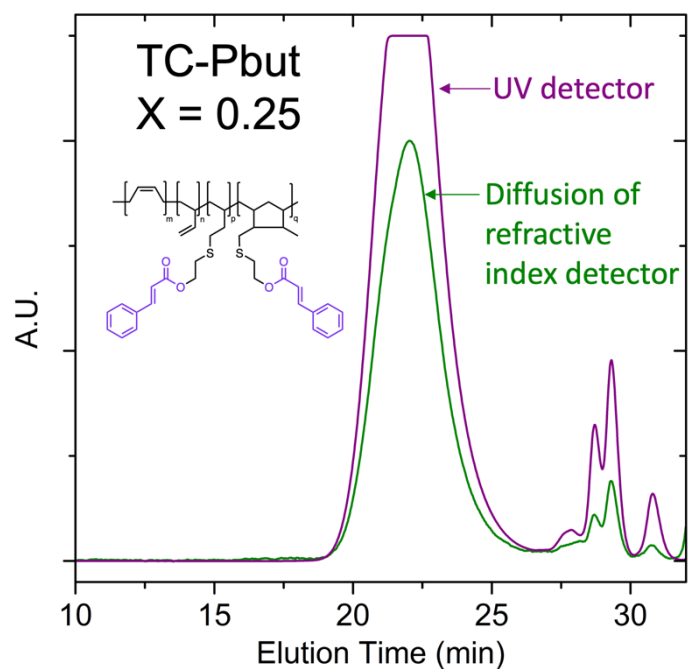


Figure S6: SEC elugram of TC-PBut, $X = 0.25$ (THF, polystyrene calibration)

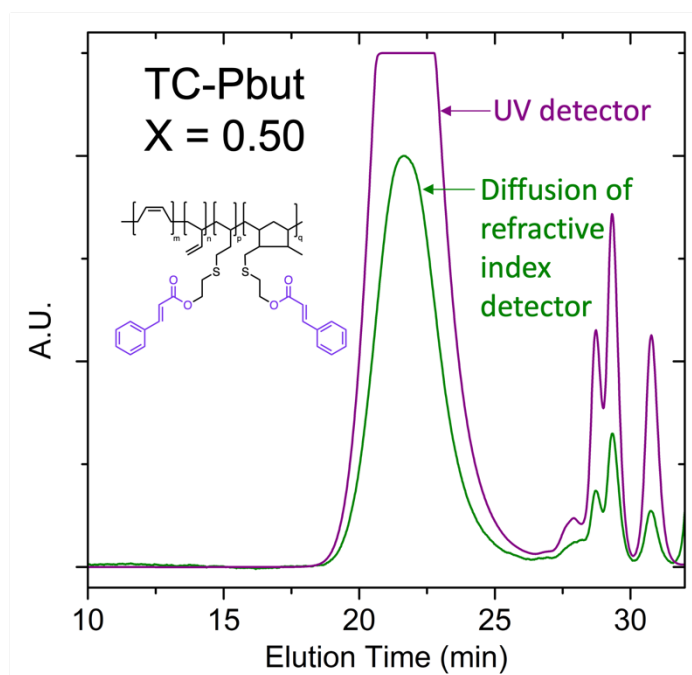


Figure S7: SEC elugram of TC-PBut, $X = 0.5$ (THF, polystyrene calibration)

VI. TGA analysis of PBut, and TC-PBut for $X = 0.25$

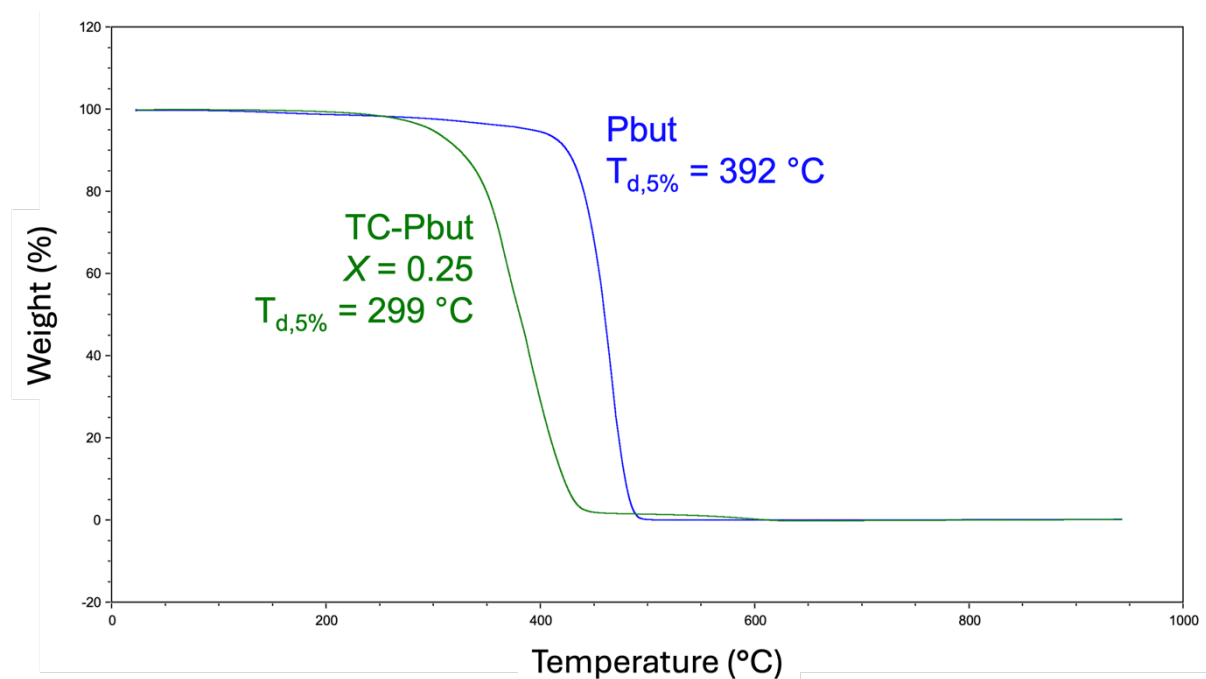


Figure S8: TGA analysis of PBut and TC-PBut, $X = 0.25$ (10 °C min^{-1} , N_2)

VII. DSC analysis of PBut, and TC-PBut for $X = 0.25$ and 0.50

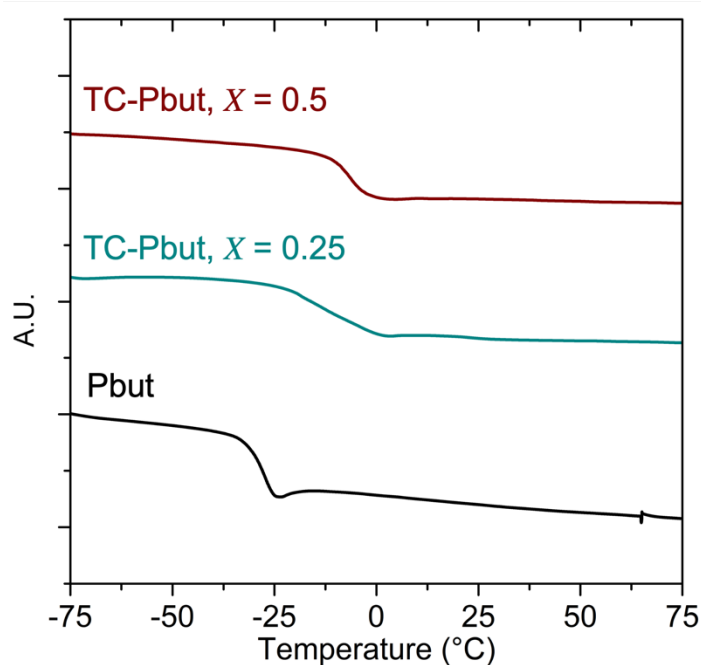


Figure S9: DSC thermograms of PBut and TC-PBut, $X = 0.5, 0.25$ (10 °C min^{-1})

VIII. Temperature profile in the UV oven

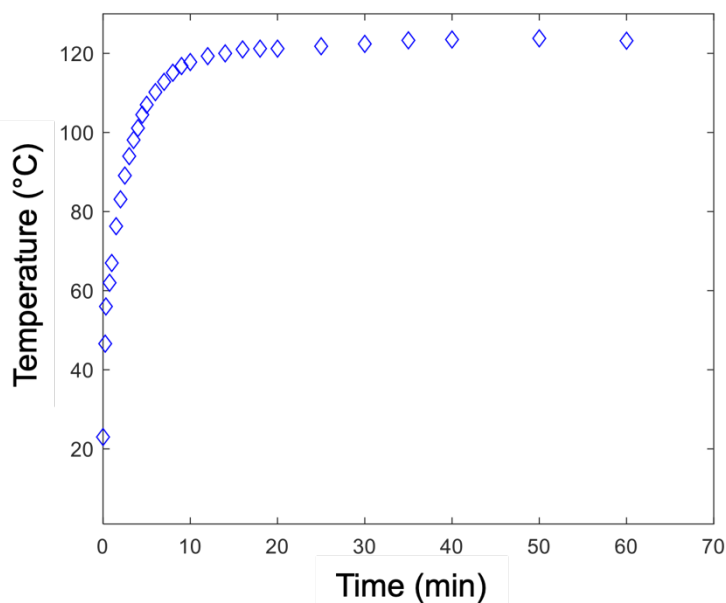


Figure S10: Temperature profile inside the UV oven (KX-314-01, Novachem[®], $\lambda = 365$ nm, 1000 mW cm^{-2}). The data are collected with a thermocouple, inside a sample photo-crosslinked at 14 cm from the LEDs.

IX. DSC thermograms of the photo-crosslinked samples

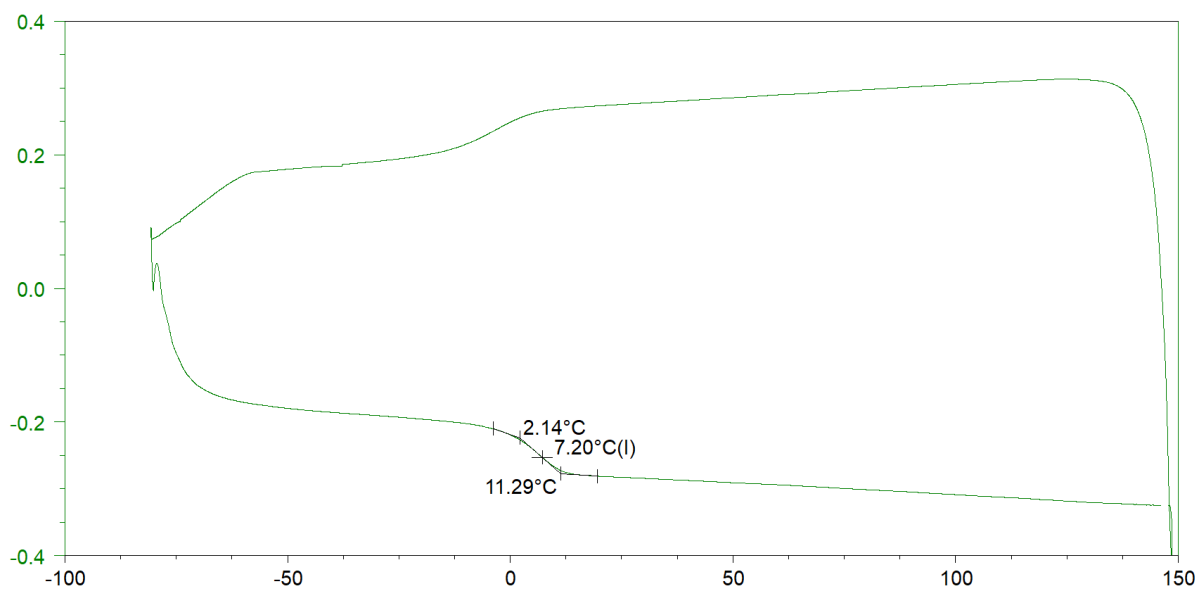


Figure S11: DSC thermograms ($10 \text{ }^\circ\text{C min}^{-1}$) of TC-PBut-10, $X = 0.5$, exposed to UV (1000 mW cm^{-2} , 14 cm) for 5 min on both sides.

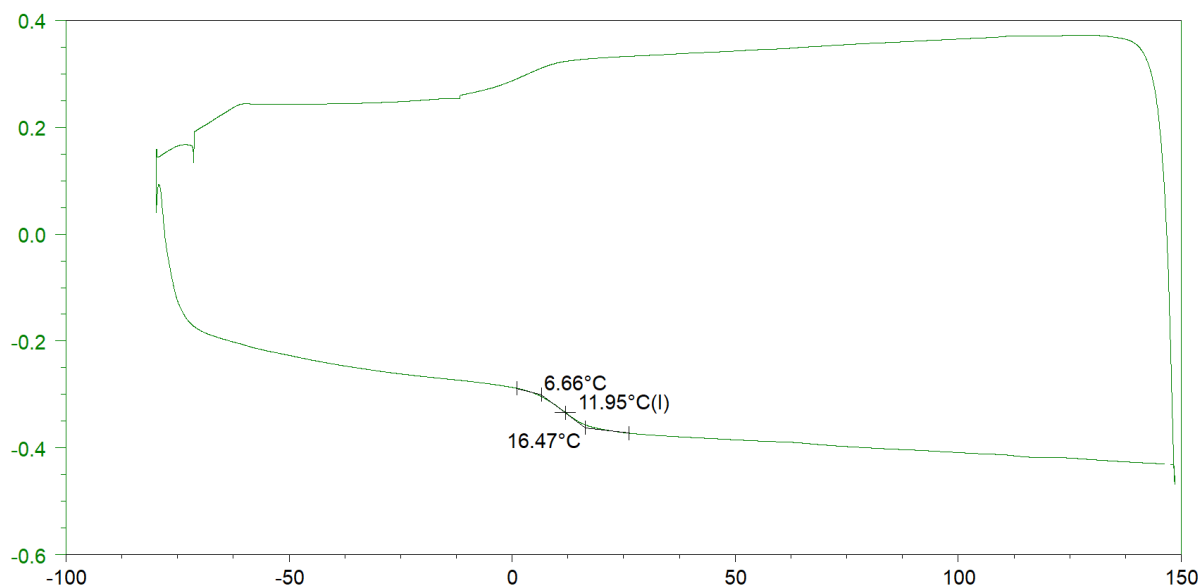


Figure S12: DSC thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$) of TC-PBut-15, $X = 0.5$, exposed to UV (1000 mW cm^{-2} , 14 cm) for 7.5 min on both sides.

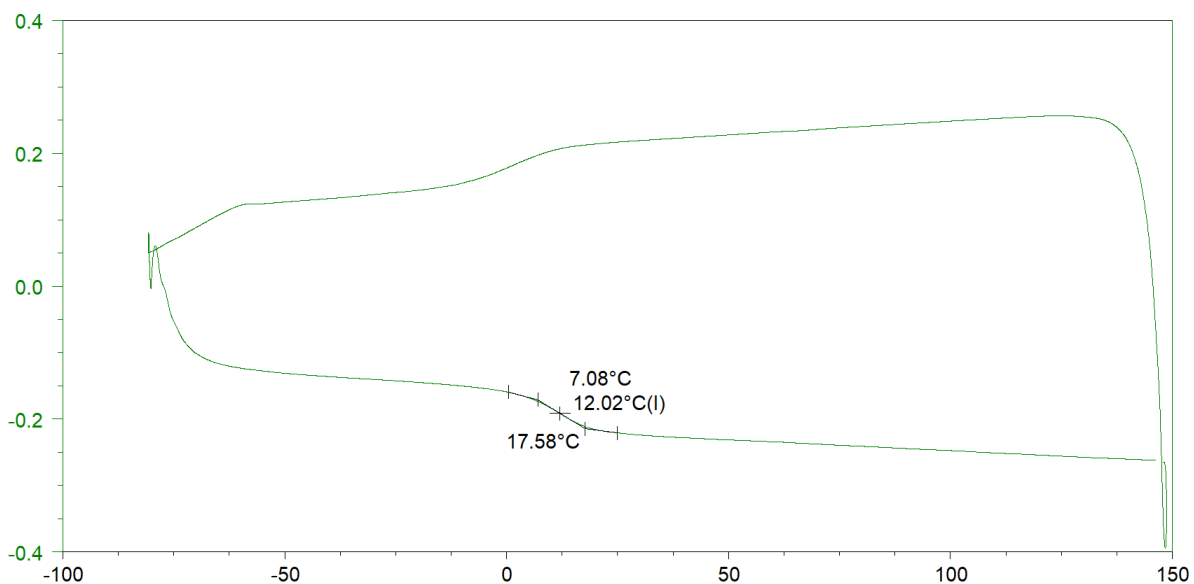


Figure S13: DSC thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$) of TC-PBut-20, $X = 0.5$, exposed to UV (1000 mW cm^{-2} , 14 cm) for 10 min on both sides.

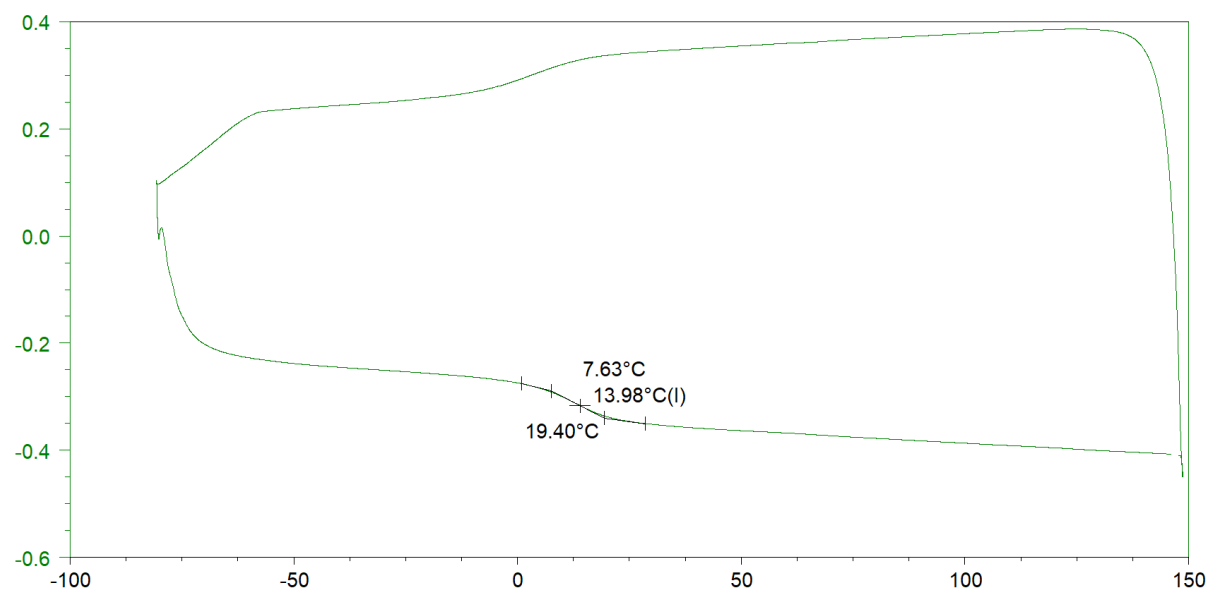


Figure S14: DSC thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$) of TC-PBut-30, $X = 0.5$, exposed to UV (1000 mW cm^{-2} , 14 cm) for 15 min on both sides.

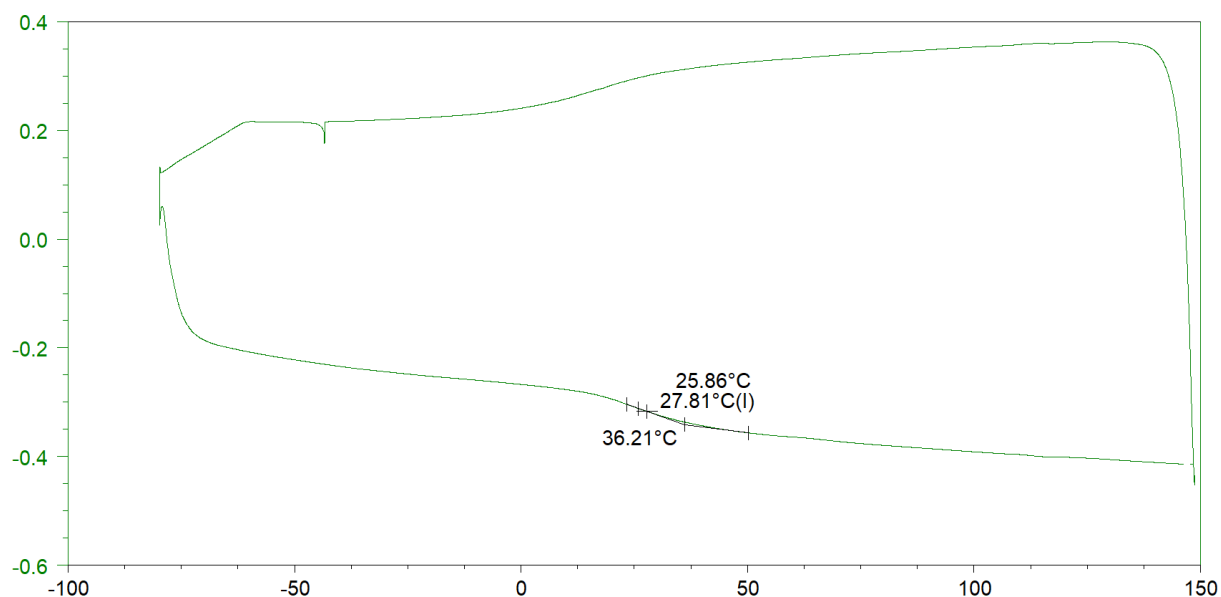


Figure S15: DSC thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$) of TC-PBut-120, $X = 0.5$, exposed to UV (1000 mW cm^{-2} , 14 cm) for 60 min on both sides.

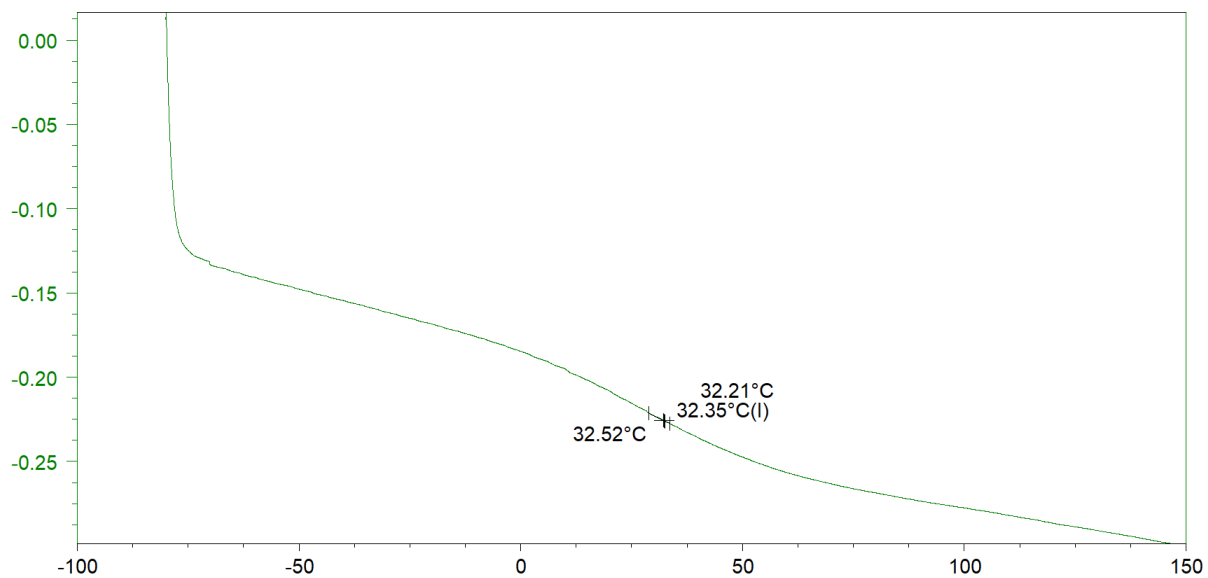


Figure S16: DSC thermograms ($10\text{ }^{\circ}\text{C min}^{-1}$) of TC-PBut-240, $X = 0.5$, exposed to UV (1000 mW cm^{-2} , 14 cm) for 120 min on both sides.

X. DMA testing of TC-PBut-15 and TC-PBut-120: frequency sweeps

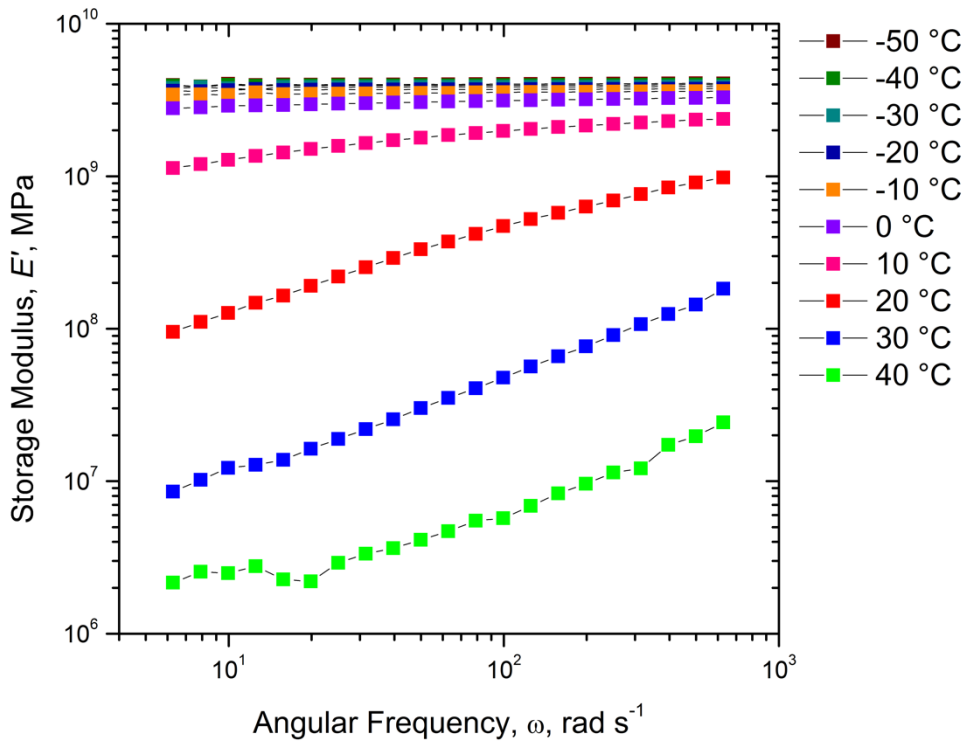


Figure S17: Frequency sweep analysis of TC-PBut-15 at various temperatures ($\epsilon = 0.005\%$)

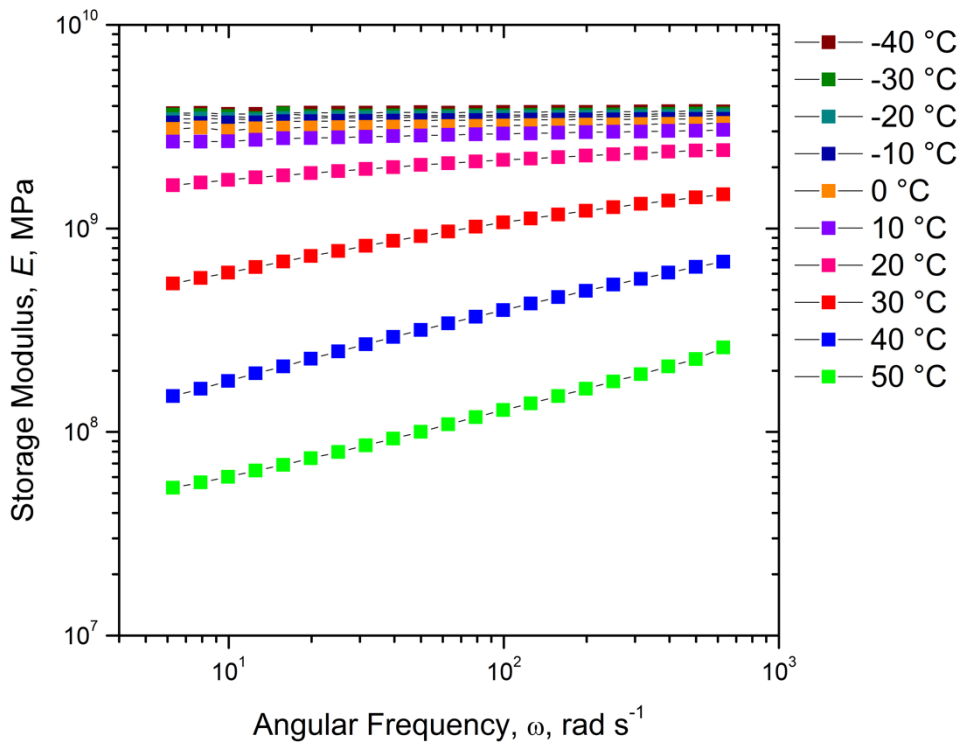


Figure S18: Frequency sweep analysis of TC-PBut-120 at various temperatures ($\epsilon = 0.005\%$)

a_T	Temperature (°C)
8.40E-04	40
0.0188351	30
0.780899	20
49.2714	10
3105.67	0
172149	-10
1.09E+07	-20
6.18E+08	-30
2.24E+10	-40
1.21E+11	-50

Table S2 : Shift factors, a_T , for the construction of the master curve of TC-PBut-15

Coefficient WLF	
c1	5.06037e15
c2	3.02189e16 K
Tref	9.89238 °C
R ²	0.996135

Table S3 : WLF coefficient for the construction of the master curve of TC-PBut-15

a_T	Température (°C)
1.98E-05	50
4.97E-04	40
0.020458	30
1.28951	20
81.2802	10
3958.08	0
231955	-10
1.37E+07	-20
8.19E+08	-30
5.04E+10	-40

Table S4 : Shift factors, a_T , for the construction of the master curve of TC-PBut-120

Coefficient WLF	
c1	195.195
c2	1164.71 K
Tref	29.9924 °C
R ²	0.999399

Table S5 : WLF coefficient for the construction of the master curve of TC-PBut-120

XI. Reduced Young's modulus maps obtained in AFM

The figures below describe the evolution of the Young's modulus over a surface of approximately $1 \mu\text{m}^2$ for each sample. The modulus value is linked to the color scale. They all suggest local inhomogeneities in cross-linking, with modulus values varying over a wide range, which account for the uncertainties in the values reported in Figure 11 of the manuscript. The values reported in Figure 11 are spatial averages taken over the entire image, performed using the Nanoscope Analysis software.

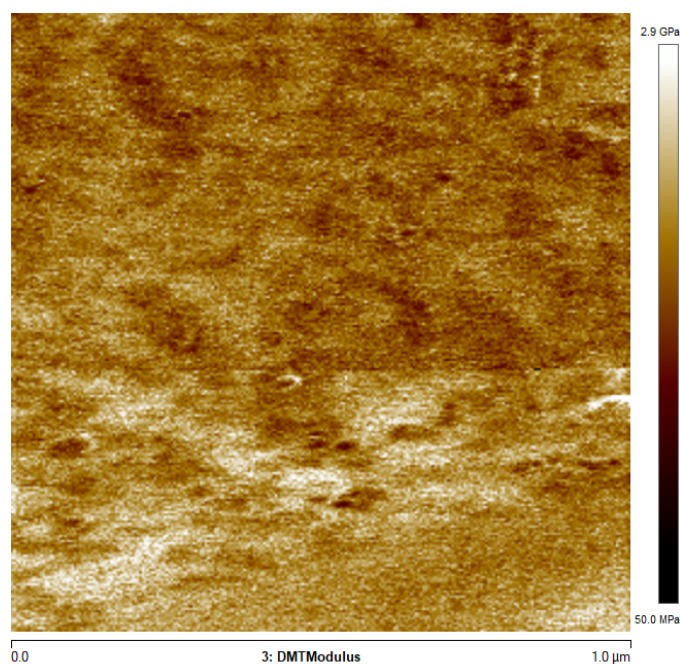


Figure S19: Reduced Young's modulus maps for TC-PBut-10, $z = 100 \mu\text{m}$

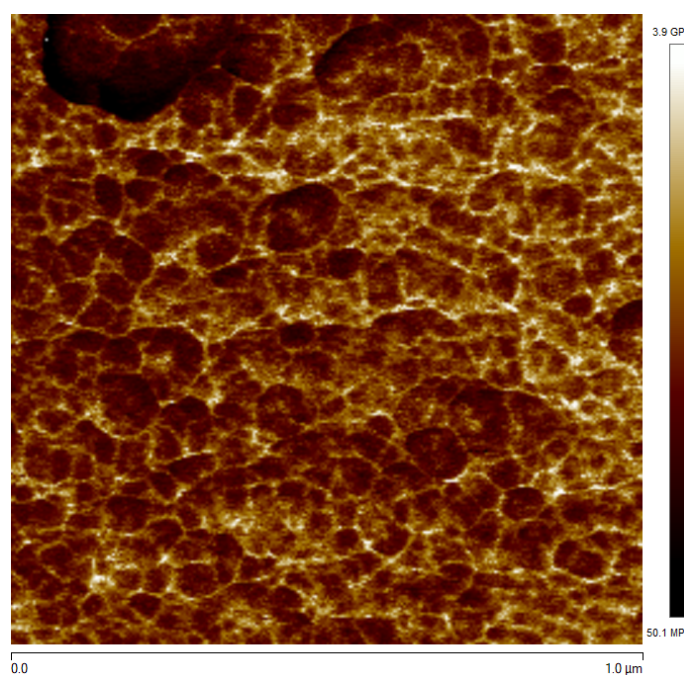


Figure S20: Reduced Young's modulus maps for TC-PBut-20, $z = 100 \mu\text{m}$

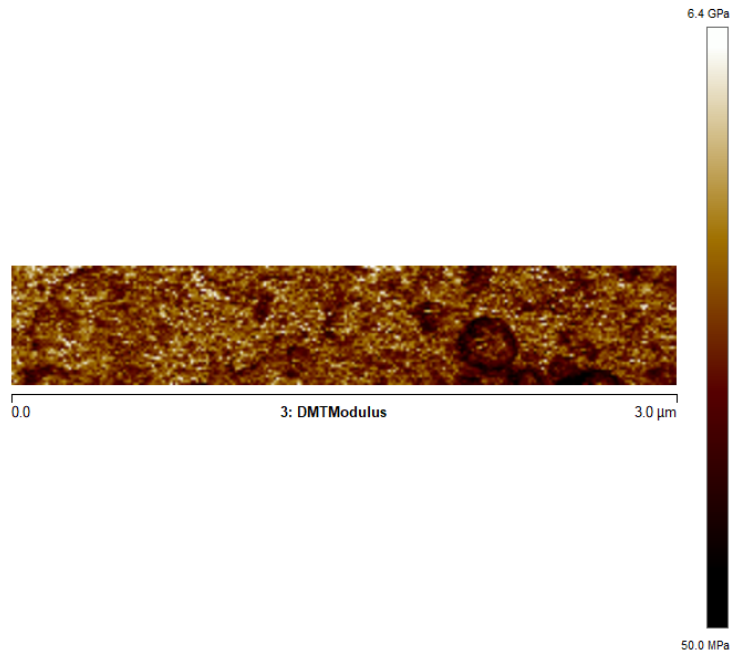


Figure S21: Reduced Young's modulus maps for TC-PBut-120, $z = 100 \mu\text{m}$

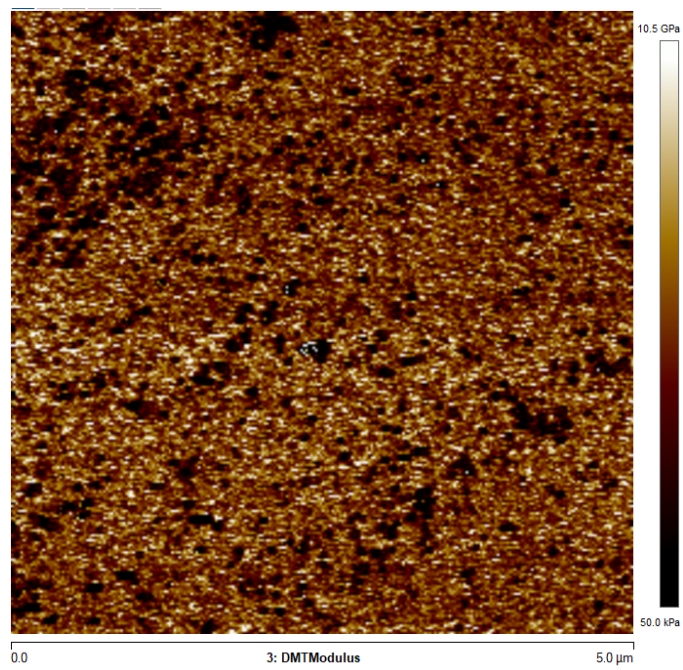


Figure S22: Reduced Young's modulus maps for TC-PBut-240, $z = 100 \mu\text{m}$

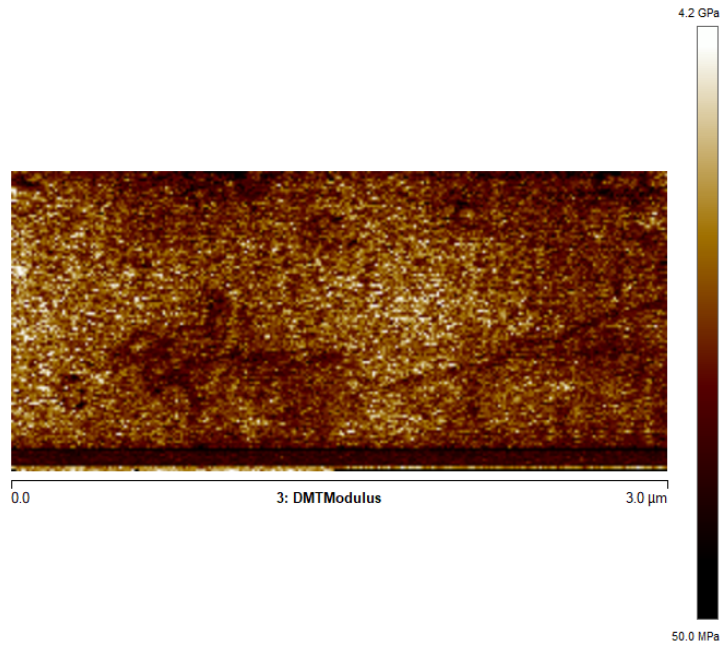


Figure S23: Reduced Young's modulus maps for TC-PBut-120, $z = 1.5$ mm

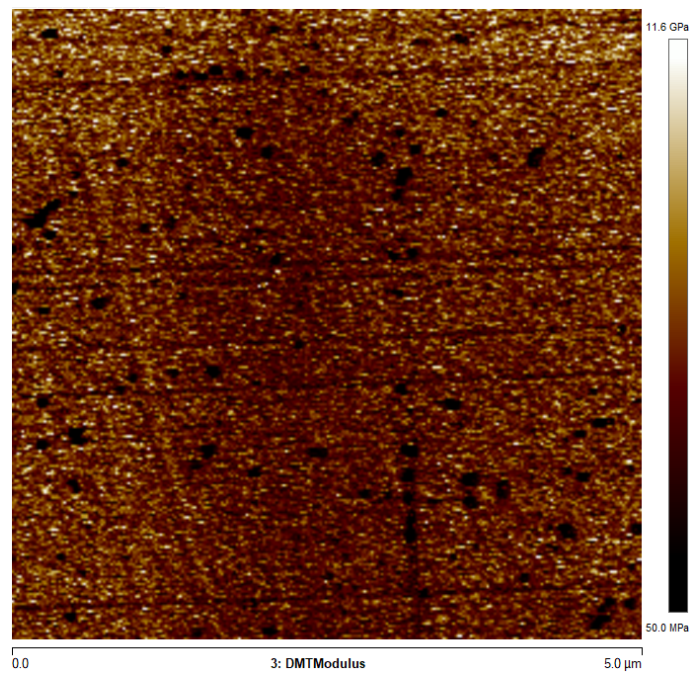


Figure S24: Reduced Young's modulus maps for TC-PBut-240, $z = 1.5$ mm