

## Supporting Information for

### A Versatile Modification Strategy to Enhance Polyethylene Properties through Solution-State Peroxide Modifications

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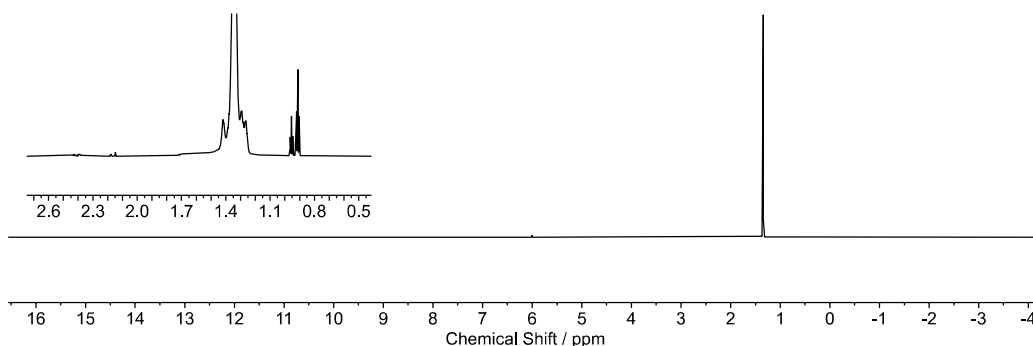
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# 1 Nuclear Magnetic Resonance (NMR) Spectroscopy Results of Injection Moulding HDPE (IMPE)

$^1\text{H}$  NMR (TCE- $d_2$ , 373 K, 800 MHz)



$^{13}\text{C}$  NMR (TCE- $d_2$ , 373 K, 201 MHz)

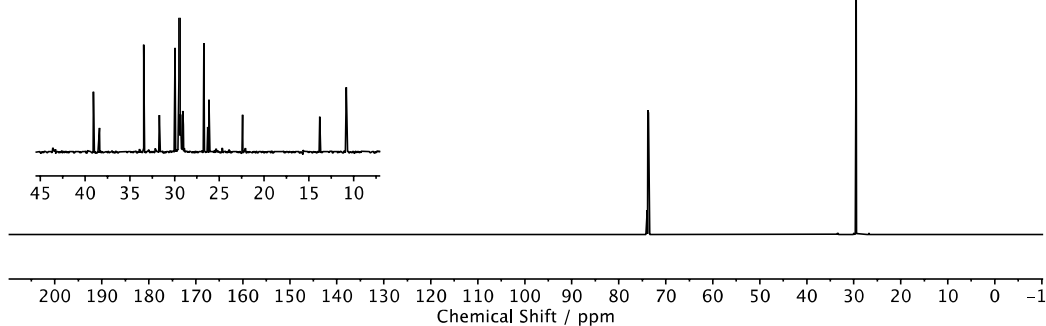


Figure S1:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of IMPE.

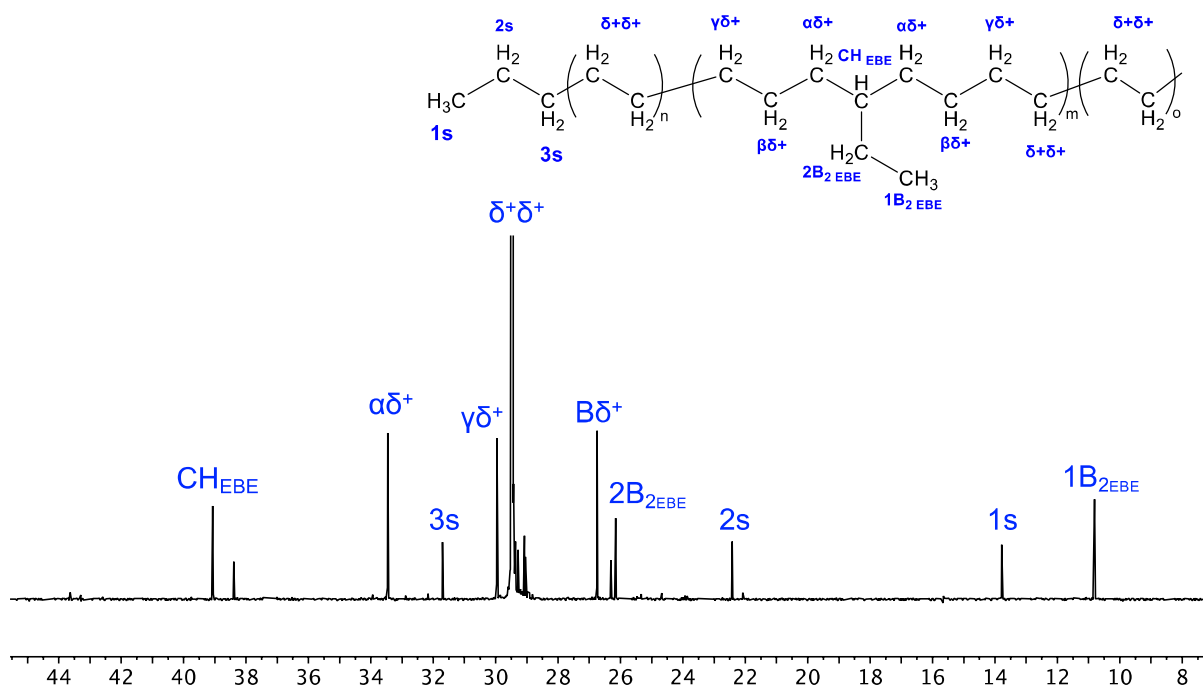


Figure S2: Assignment of the  $^{13}\text{C}$  NMR spectrum of IMPE in accordance with literature.<sup>1</sup>

**Table S1:** A summary of the  $^{13}\text{C}$  NMR spectrum results for **IMPE**.

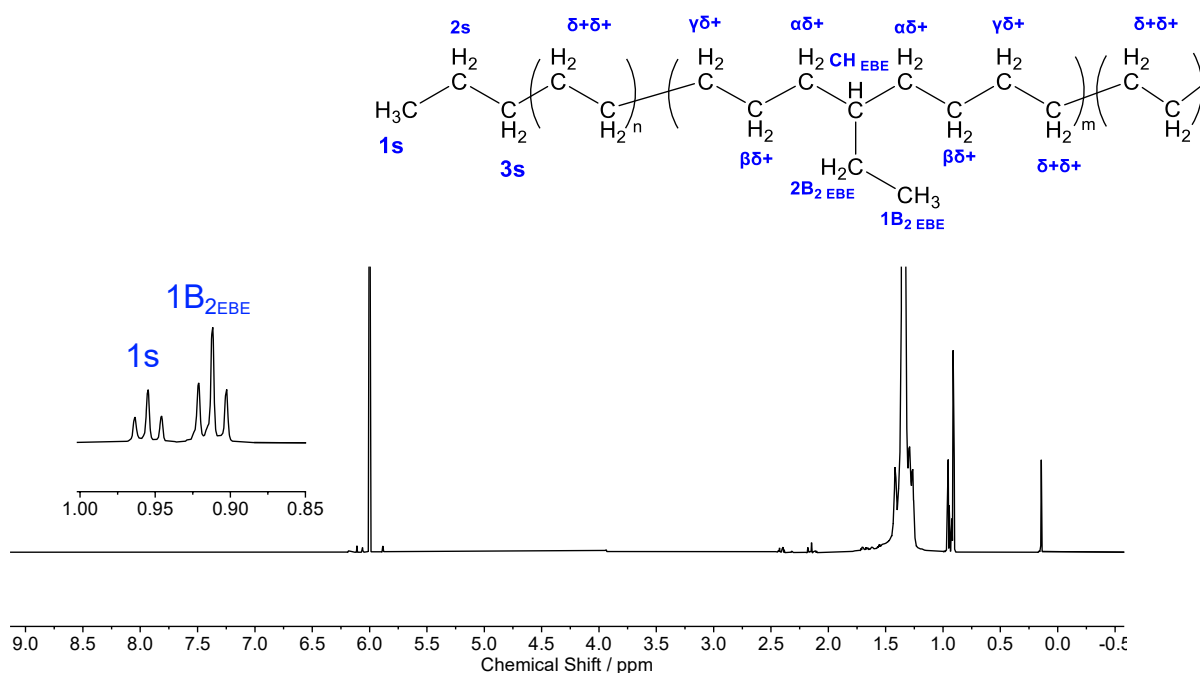
$^{13}\text{C}$ Peak (ppm)	Integral <sup>a</sup>	Moiety	Origin monomer
10.8	4.26	$\text{CH}_3$	Butene
13.8	2.00	$\text{CH}_3$	Ethylene
22.4	1.96	$\text{CH}_2$	Ethylene
26.2	4.10	$\text{CH}_2$	Butene
26.8	7.89	$\text{CH}_2$	Ethylene
29.5	1270.45	$\text{CH}_2$	Ethylene
30	7.93	$\text{CH}_2$	Ethylene
31.7	2.03	$\text{CH}_2$	Ethylene
33.5	8.04	$\text{CH}_2$	Butene and Ethylene <sup>b</sup>
39.1	3.98	$\text{CH}$	Butene

<sup>a</sup> The integral value of 1s peak was set to 2 as an ideal polymer chain would have two  $\text{CH}_3$  end groups. <sup>b</sup> 4.02 area under signal each.

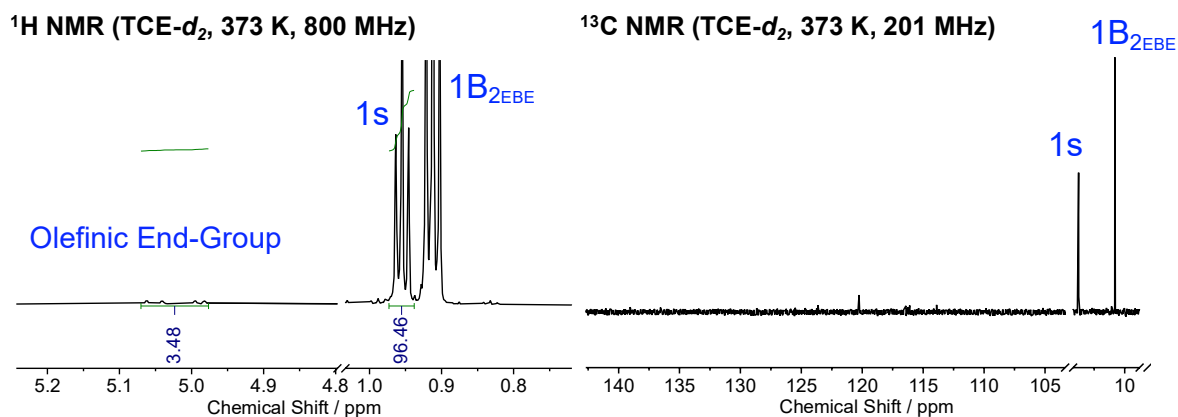
**Calculation S1:** Estimating the 1-butene comonomer content in **IMPE** in accordance with the  $^{13}\text{C}$  NMR results.

$$\text{1-Butene mol\%} = (\text{Sum of Peak Integrals Originating from 1-Butene Monomer}) / (\text{Sum of All Integrals}) * 100$$

$$\text{1-Butene mol\%} = 1.2 \text{ mol\%}$$



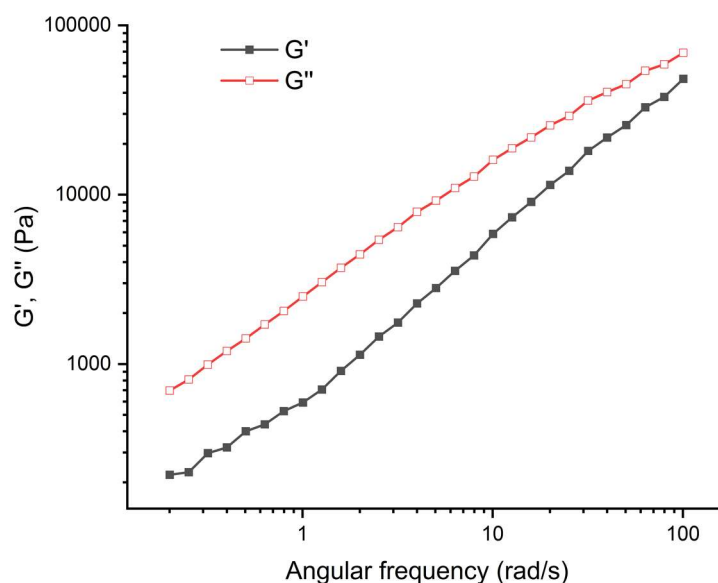
**Figure S3:** Assignment of the  $^1\text{H}$  NMR spectrum of **IMPE** in accordance with literature.<sup>1</sup> The peak at 6.0 ppm originates from the NMR solvent.



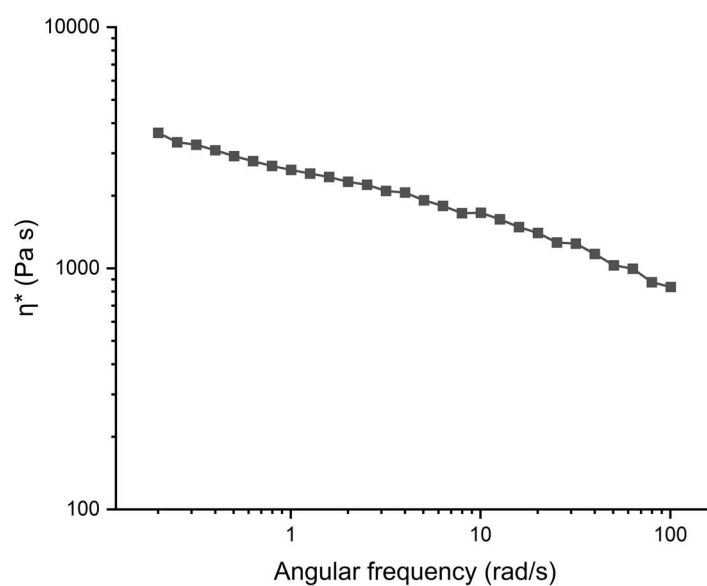
**Figure S4:** Investigating for the presence of olefinic end-groups in IMPE. While a small amount of olefinic units were identified in the proton NMR, it was not possible to identify any olefinic carbons with  $^{13}\text{C}$  NMR spectroscopy. This figure shows that the amount of any olefin end-group is very low, and most chains are fully saturated.

## 2 Linear Rheological Characterisation of the Commercial and Modified Samples

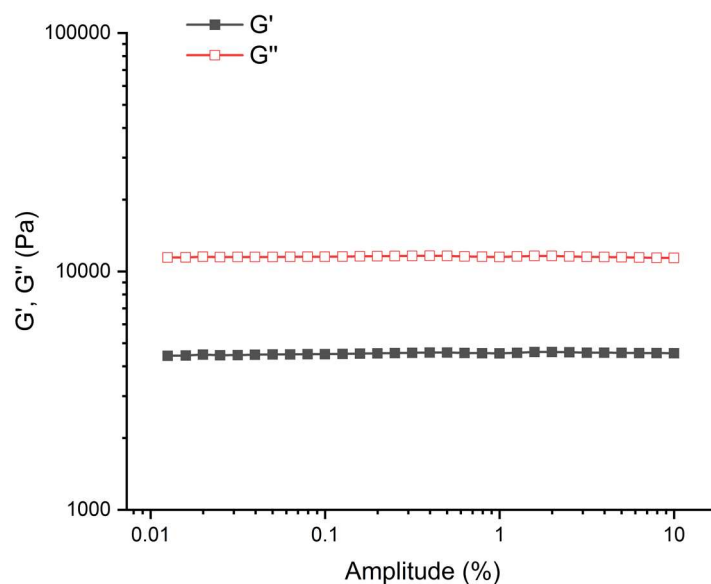
- IMPE



**Figure S5:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for the injection-moulding grade polymer.

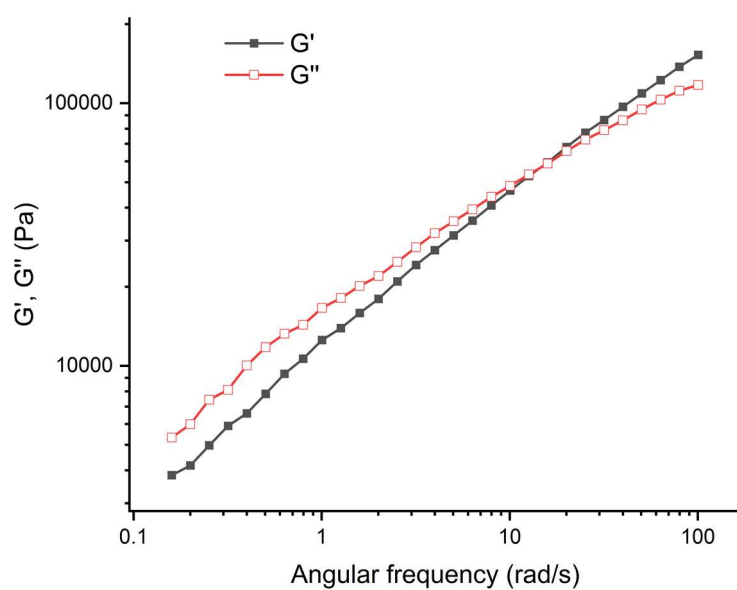


**Figure S6:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for the injection-moulding grade polymer.

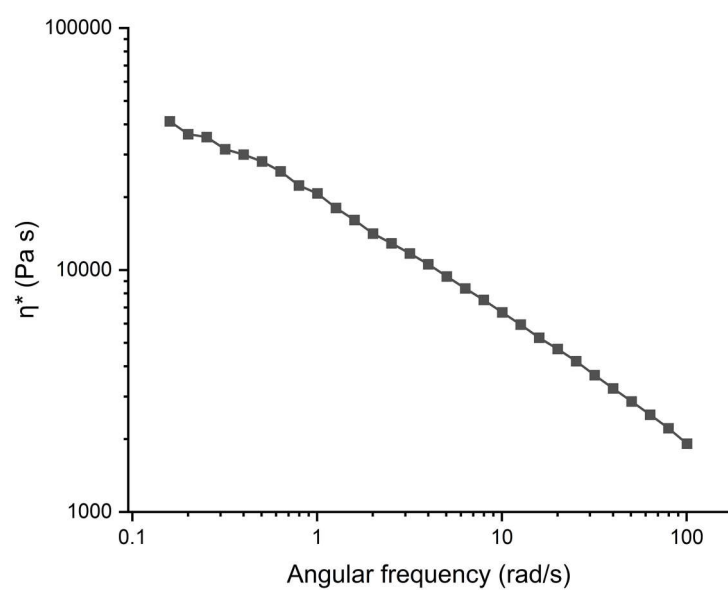


**Figure S7:** The amplitude sweep test (at 1 Hz, 190 °C) on IMPE showing how dynamic moduli behave as a function of amplitude (strain), confirming the earlier frequency sweep measurement was performed at the linear viscoelastic regime (LVER).

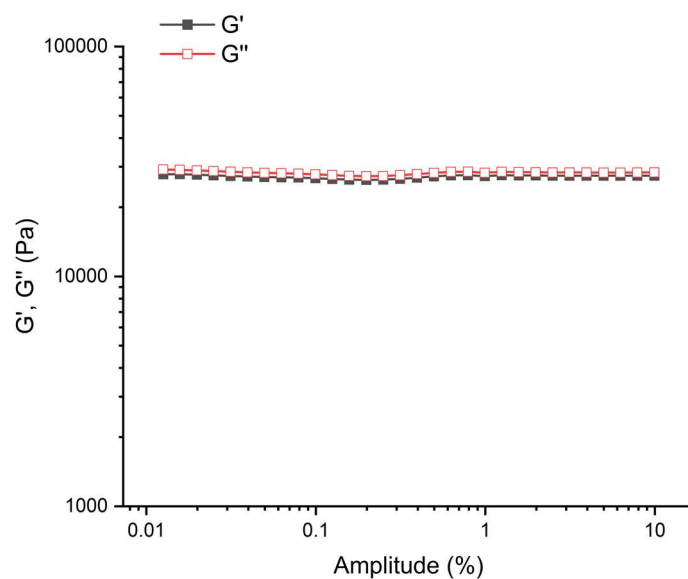
- **Blow Moulding HPDE (BMPE)**



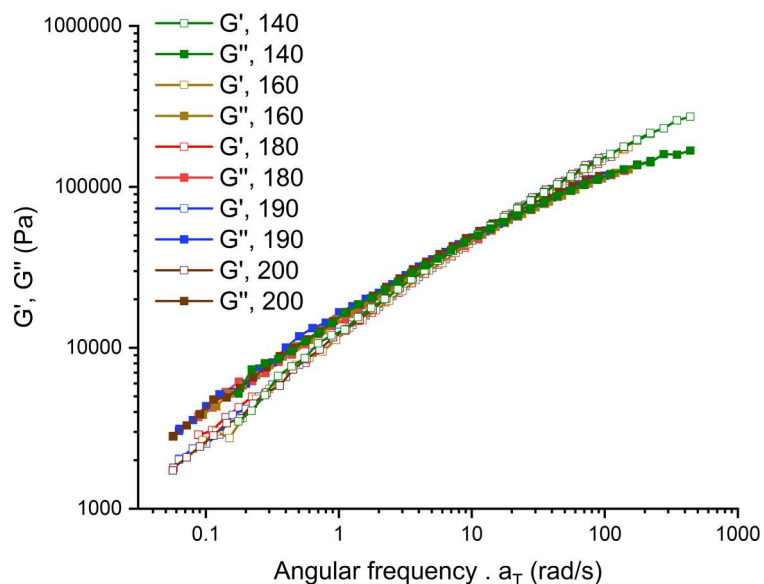
**Figure S8:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for the blow-moulding grade polymer.



**Figure S9:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for the blow-moulding grade polymer.

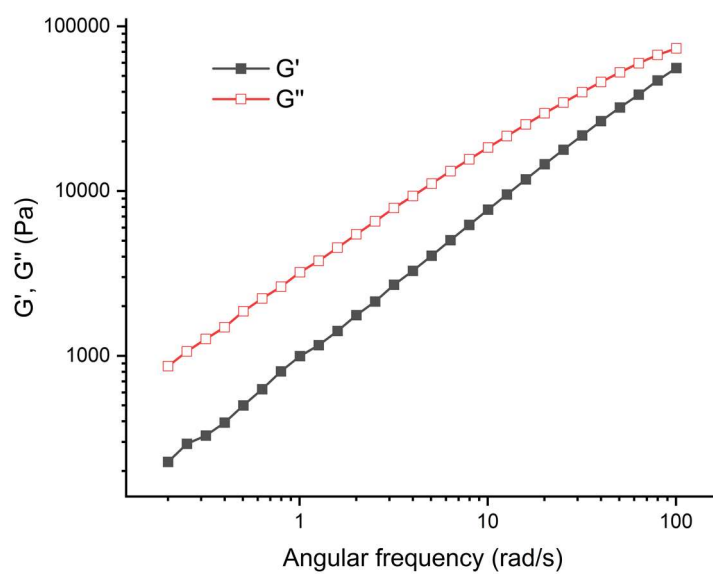


**Figure S10:** The amplitude sweep test (at 1 Hz, 190 °C) on **BMPE** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

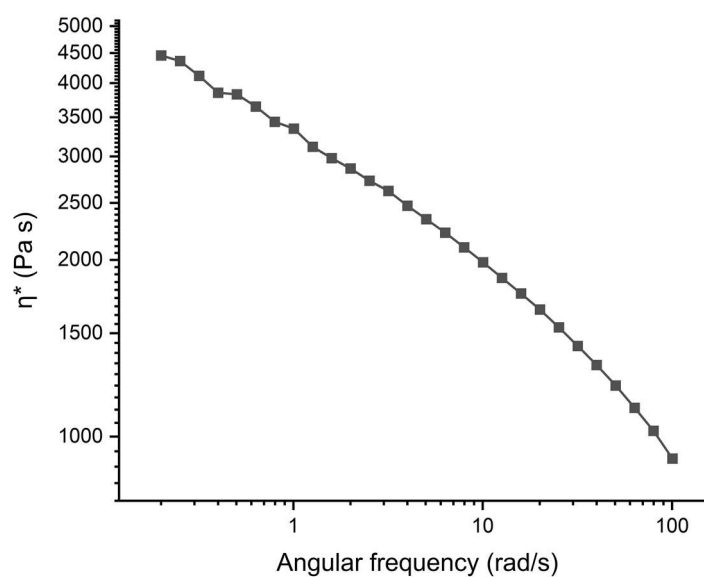


**Figure S11:** Time-temperature superposition (TTS) of the frequency dependencies of the dynamic moduli at the reference temperature of 190 °C (all at 1% amplitude). The shift factors ( $a_T$ ) were determined as 0.9 at 200 °C, 1.4 at 180 °C, 1.5 at 160 °C and 2.2 at 140 °C.

- **M1**

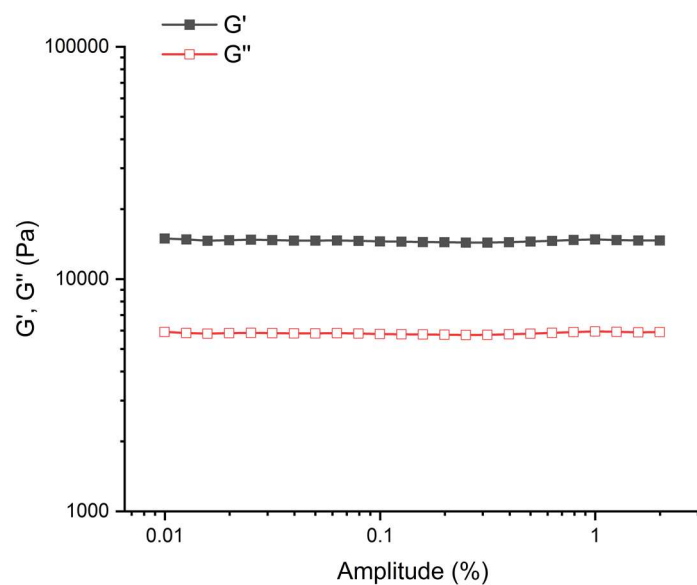


**Figure S12:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M1**.



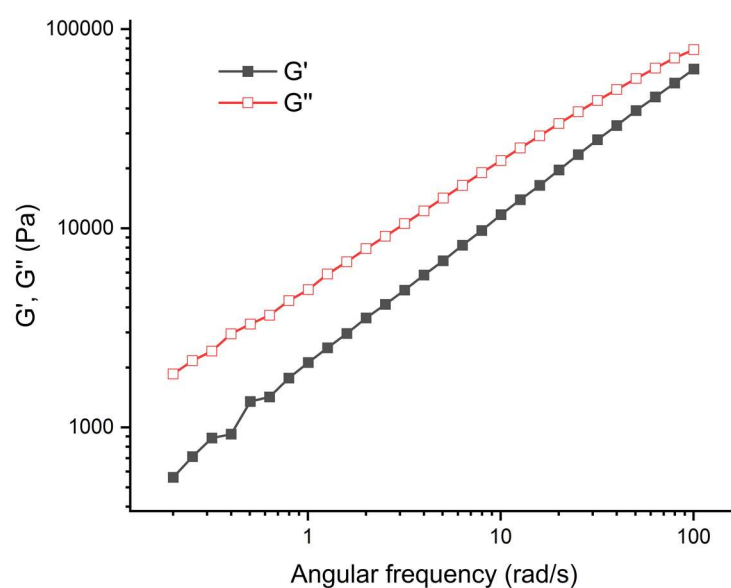
**Figure S13:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M1**.



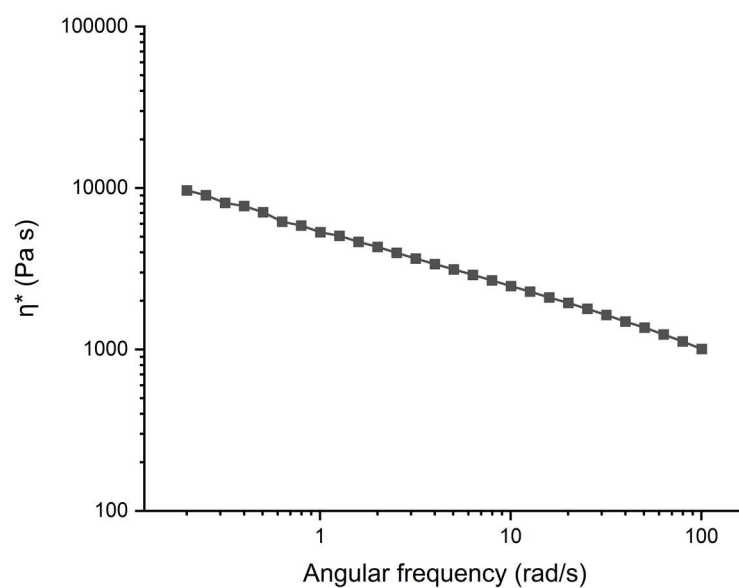


**Figure S14:** The amplitude sweep test (at 1 Hz, 190 °C) on **M1** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

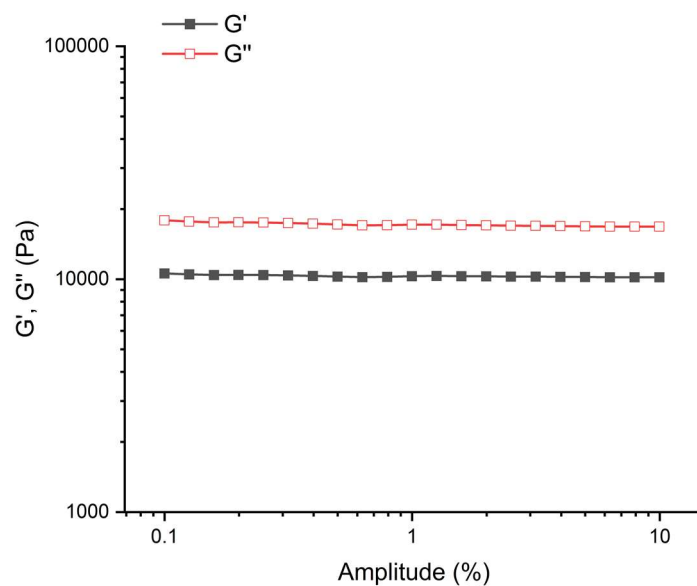
- **M2**



**Figure S15:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M2**.

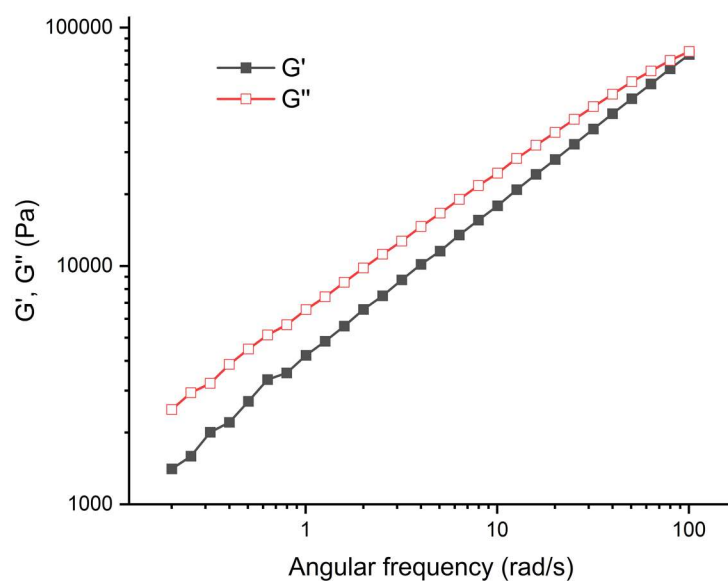


**Figure S16:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M2**.

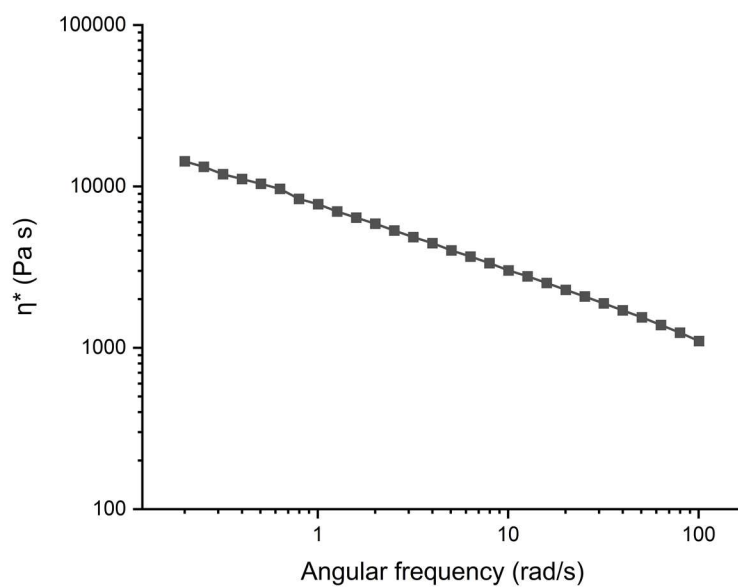


**Figure S17:** The amplitude sweep test (at 1 Hz, 190 °C) on **M2** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

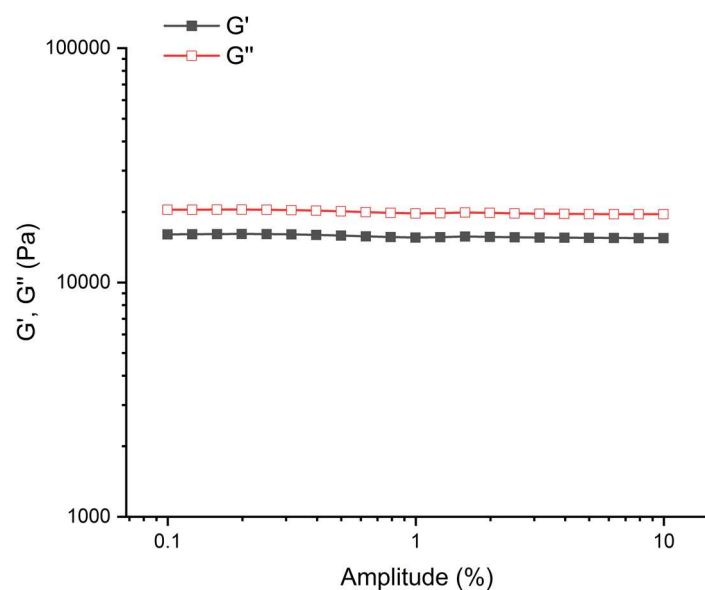
- **M3**



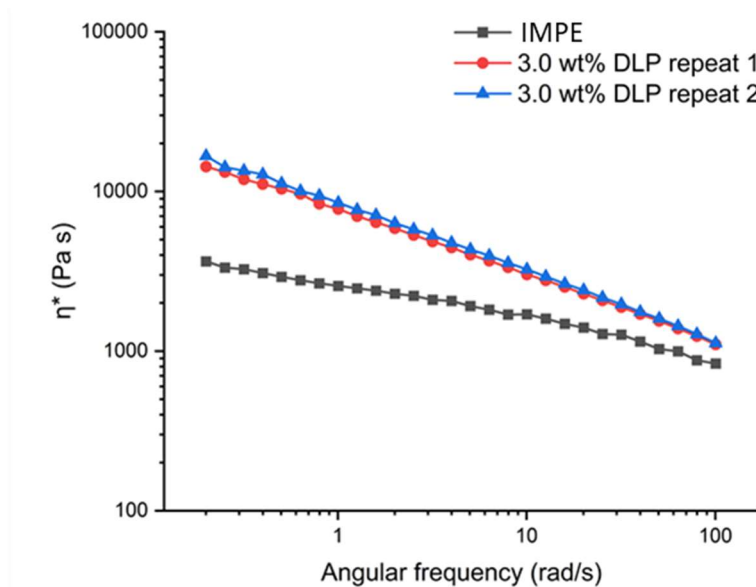
**Figure S18:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M3**.



**Figure S19:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M3**.

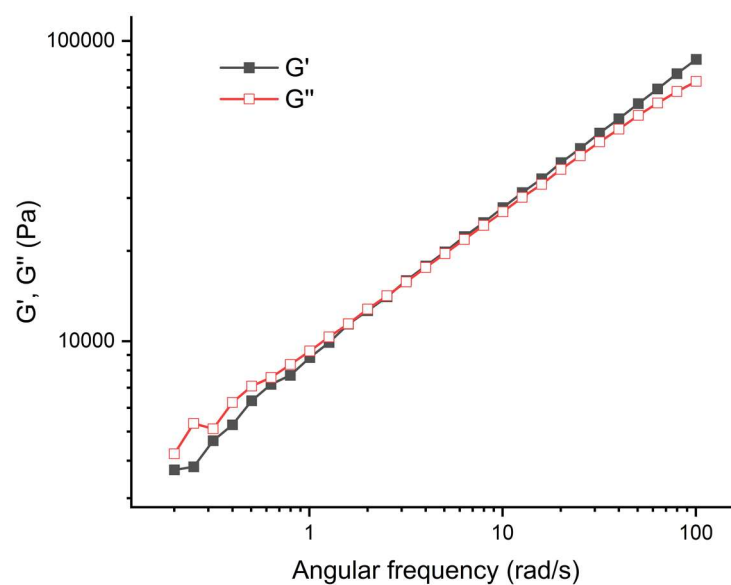


**Figure S20:** The amplitude sweep test (at 1 Hz, 190 °C) on **M3** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

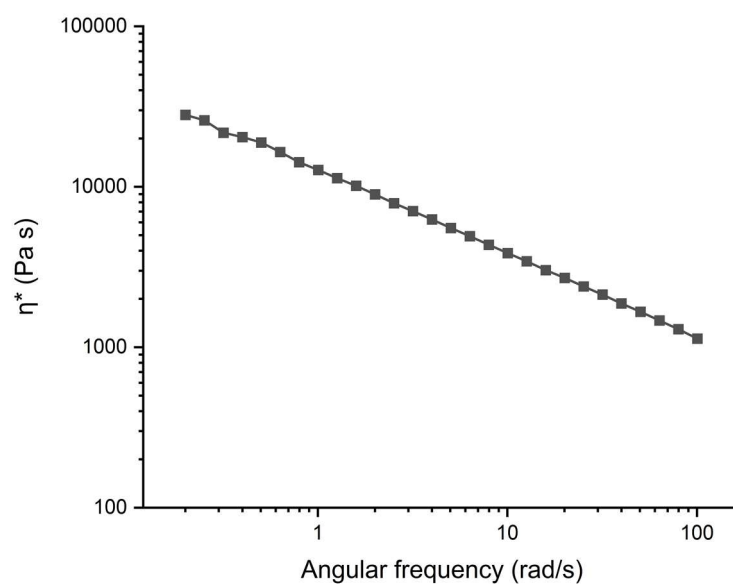


**Figure S21:** Frequency dependencies of the complex viscosity values for two separately prepared samples using the same experimental conditions (at 1% amplitude, 190 °C). The error on each data point was less than 5% on average.

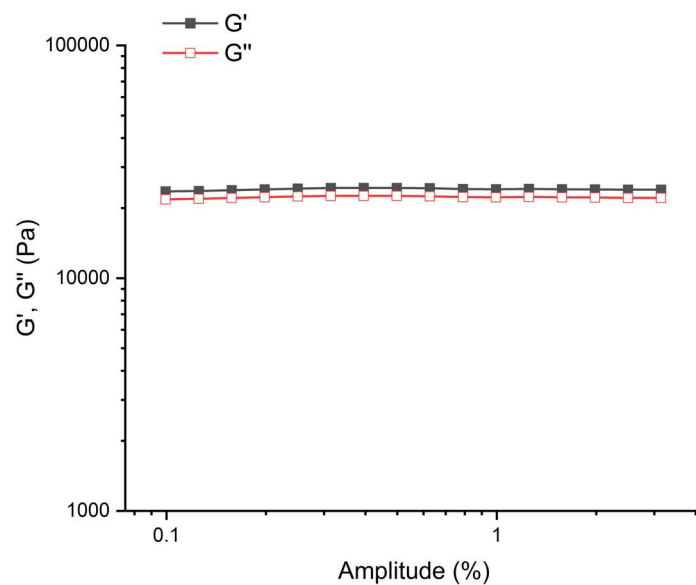
- **M4**



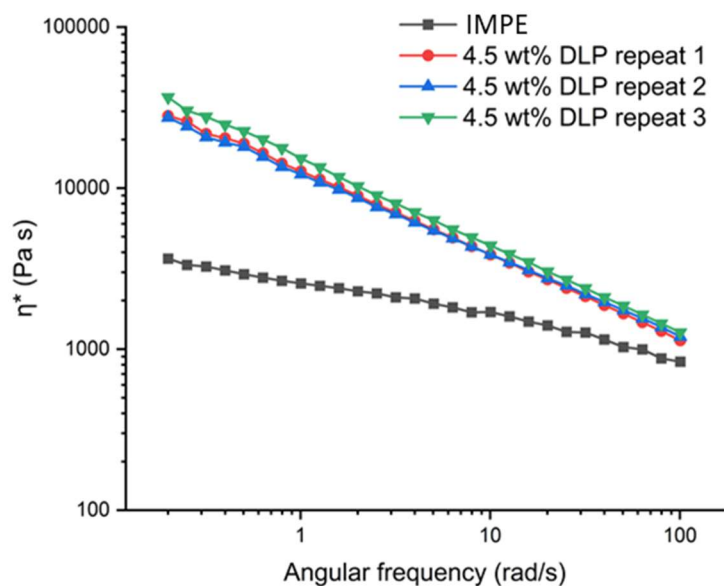
**Figure S22:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M4**.



**Figure S23:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M4**.

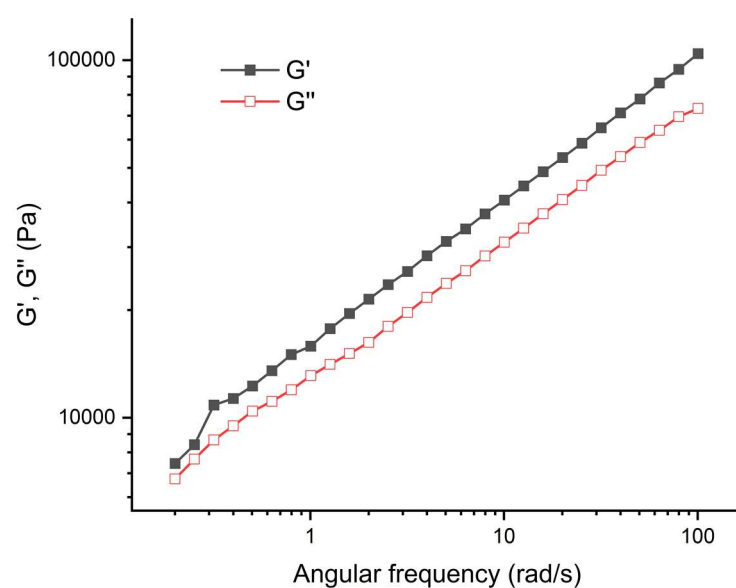


**Figure S24:** The amplitude sweep test (at 1 Hz, 190 °C) on **M4** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

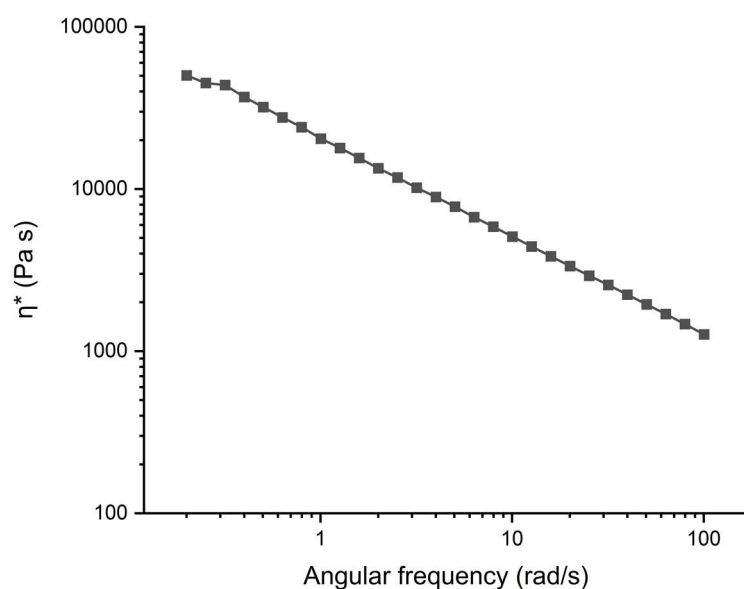


**Figure S25:** Frequency dependencies of the complex viscosity values for three separately prepared samples using the same experimental conditions (at 1% amplitude, 190 °C). The error on each data point was less than 5% on average.

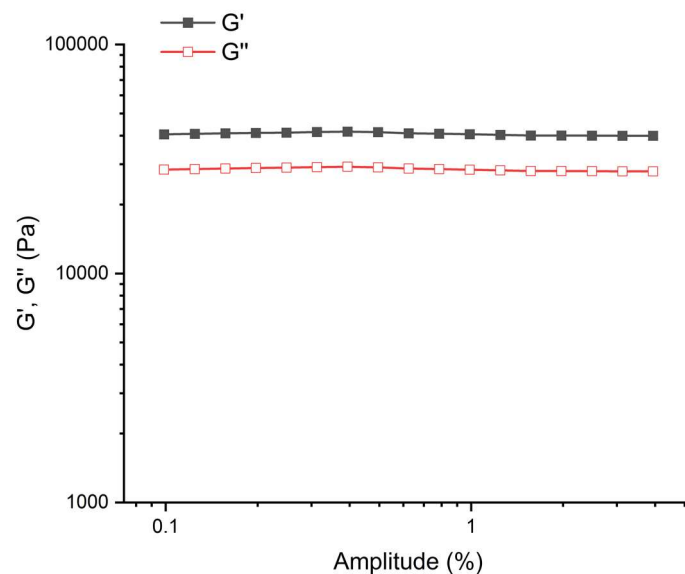
- **M5**



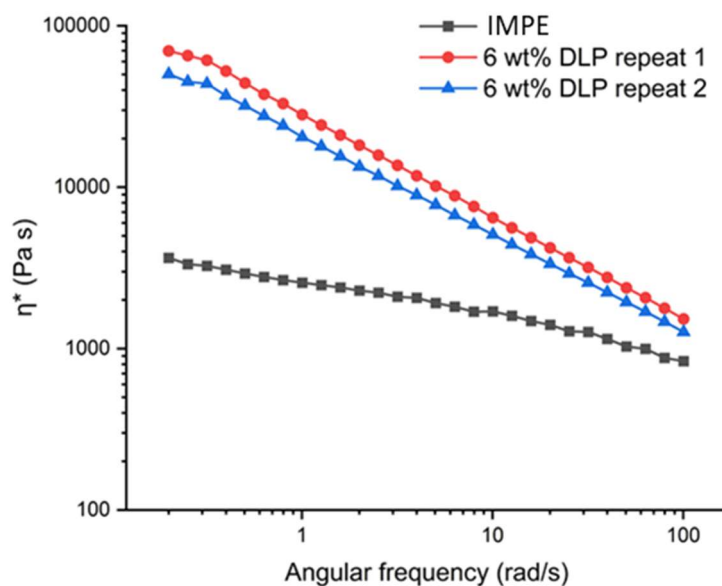
**Figure S26:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M5**.



**Figure S27:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M5**.

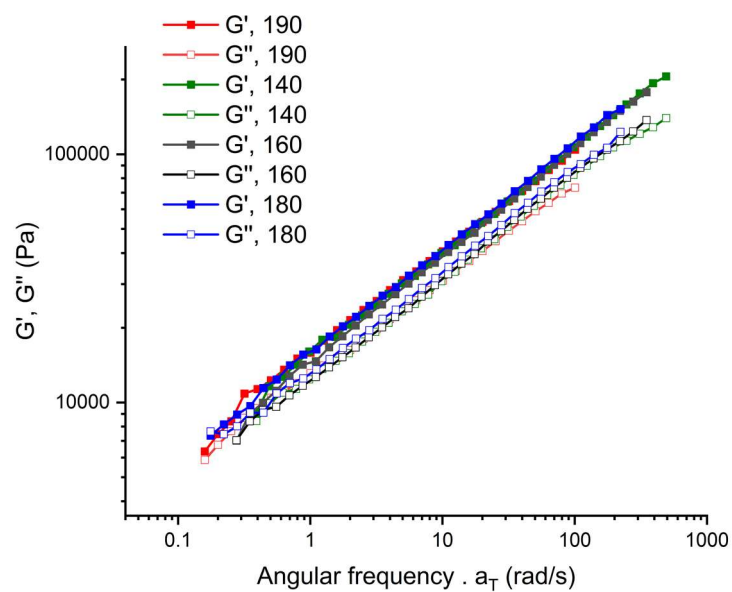


**Figure S28:** The amplitude sweep test (at 1 Hz, 190 °C) on **M5** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.



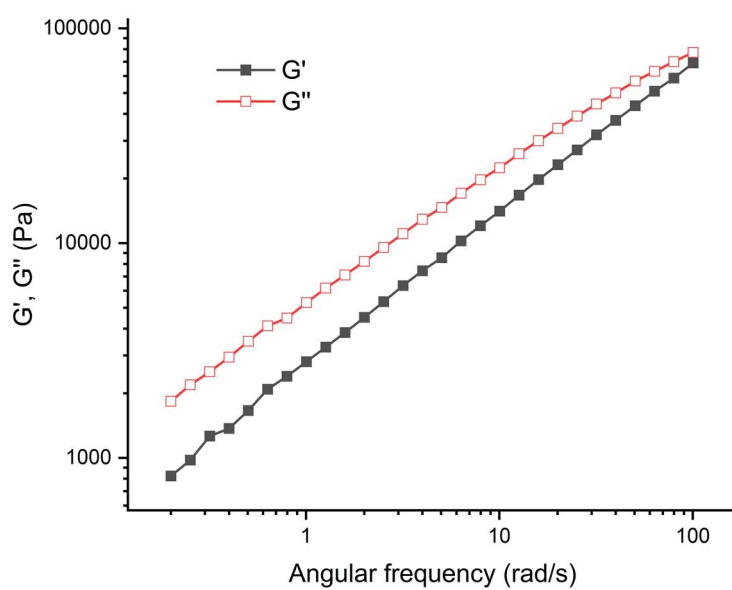
**Figure S29:** Frequency dependencies of the complex viscosity values for two separately prepared samples using the same experimental conditions (at 1% amplitude, 190 °C). The error on each data point was less than 10% on average.



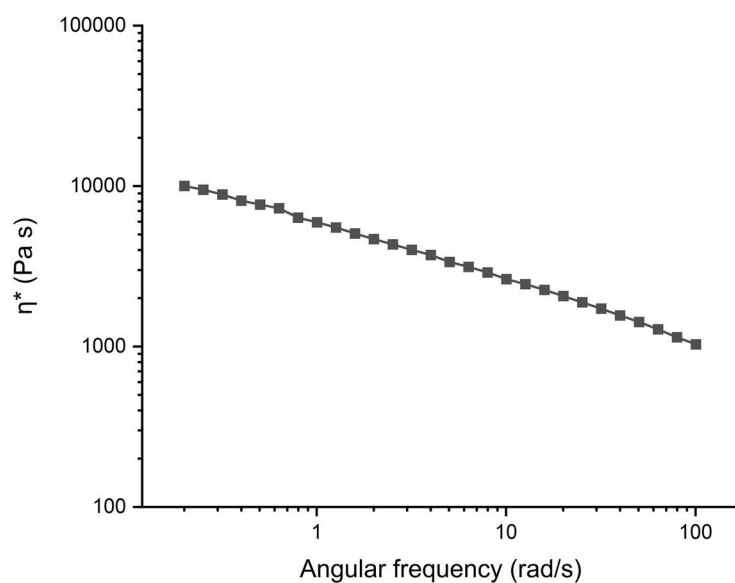


**Figure S30:** TTS of the frequency dependencies of the dynamic moduli at the reference temperature of 190 °C (all at 1% amplitude). The shift factors ( $a_T$ ) were determined as 1.4 at 180 °C, 2.2 at 160 °C and 3.1 at 140 °C.

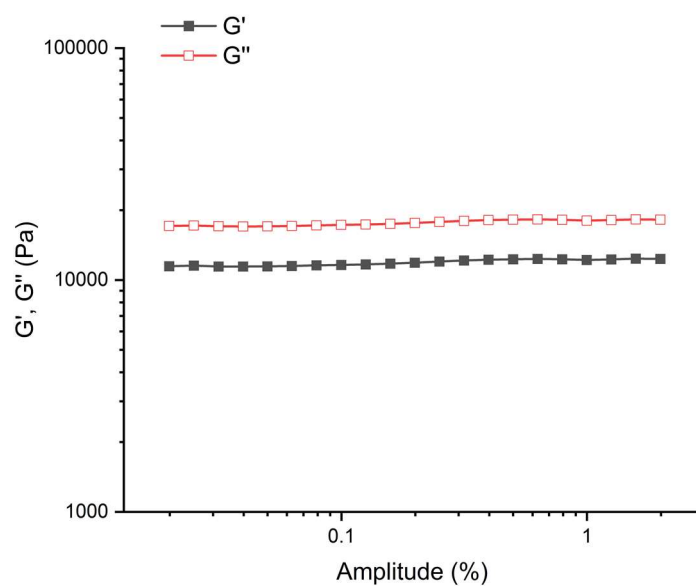
- **M6**



**Figure S31:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M6**.

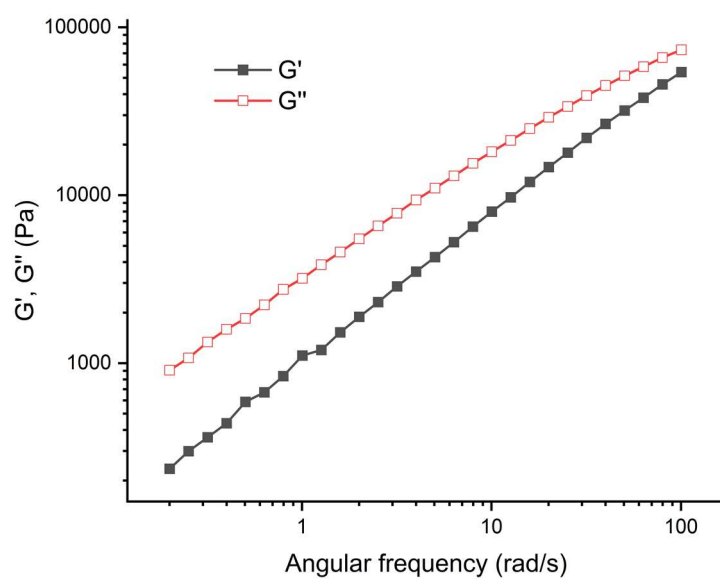


**Figure S32:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M6**.

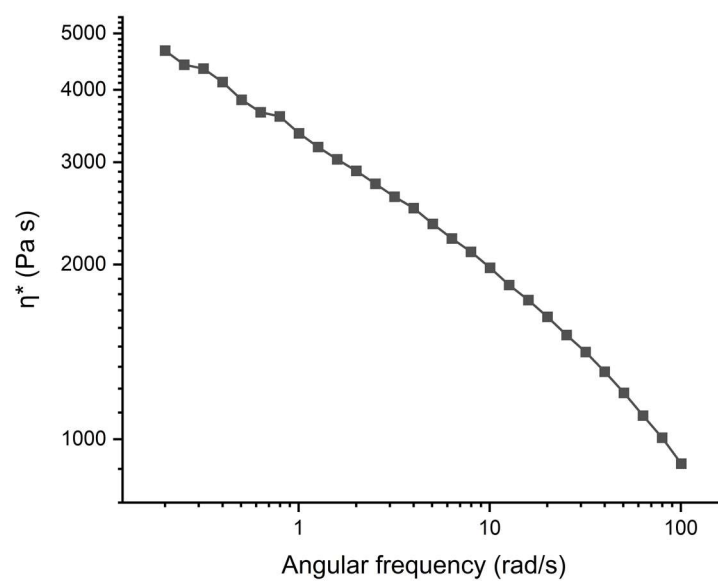


**Figure S33:** The amplitude sweep test (at 1 Hz, 190 °C) on **M6** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

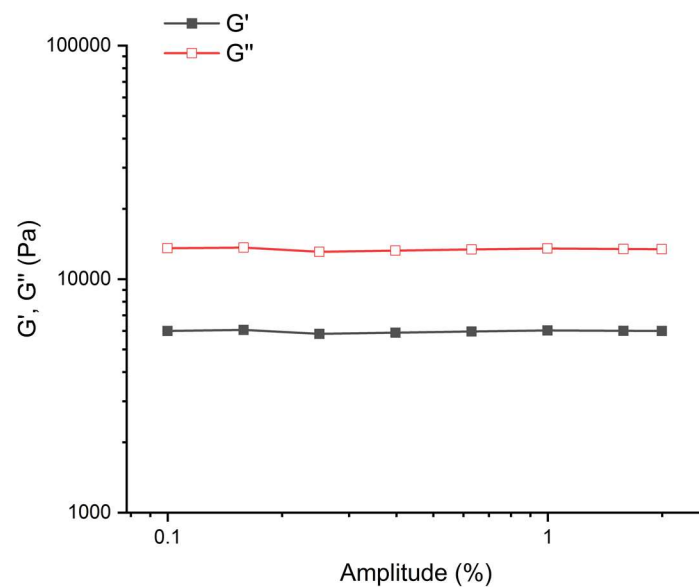
- **M7**



**Figure S34:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M7**.

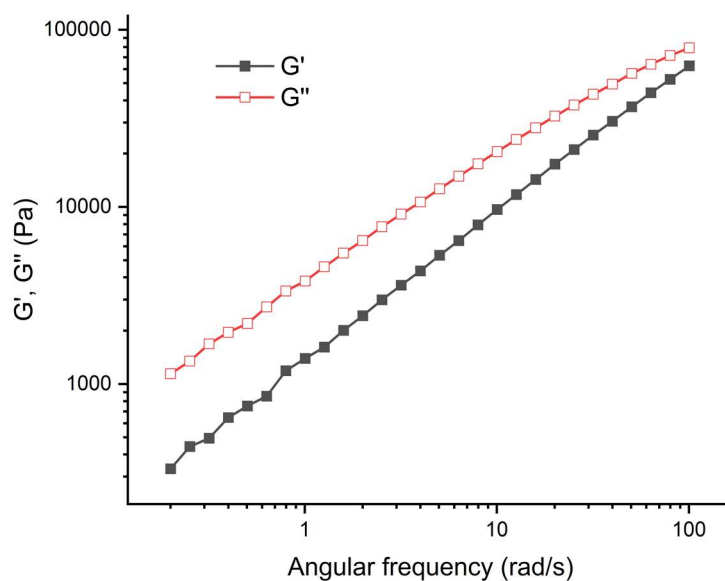


**Figure S35:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M7**.

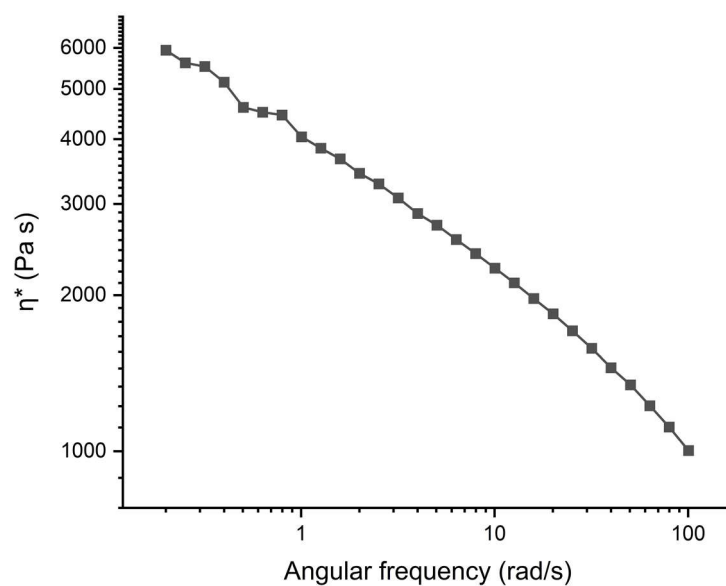


**Figure S36:** The amplitude sweep test (at 1 Hz, 190 °C) on **M7** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

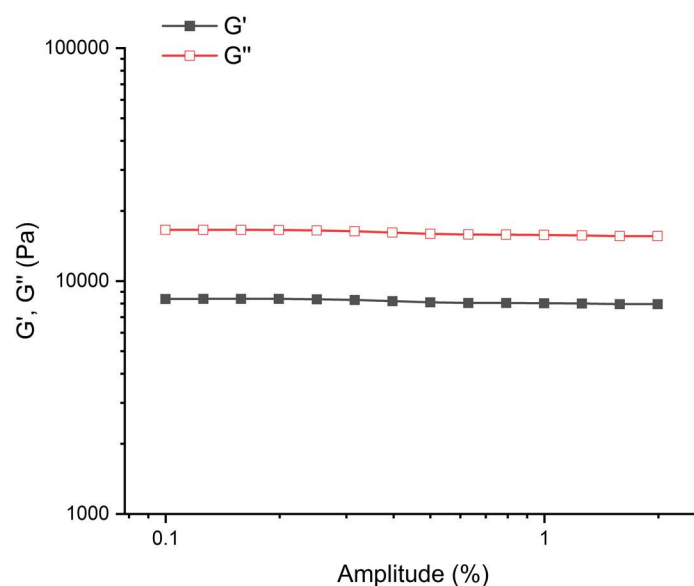
- **M8**



**Figure S37:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M8**.

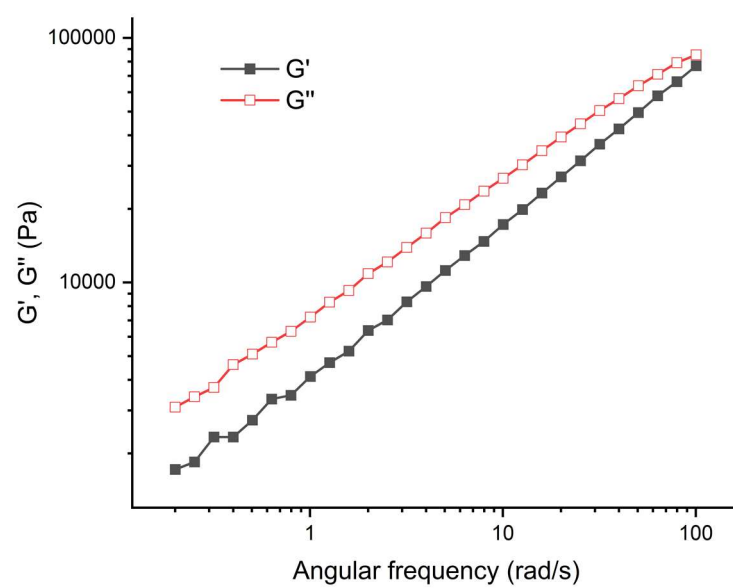


**Figure S38:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M8**.

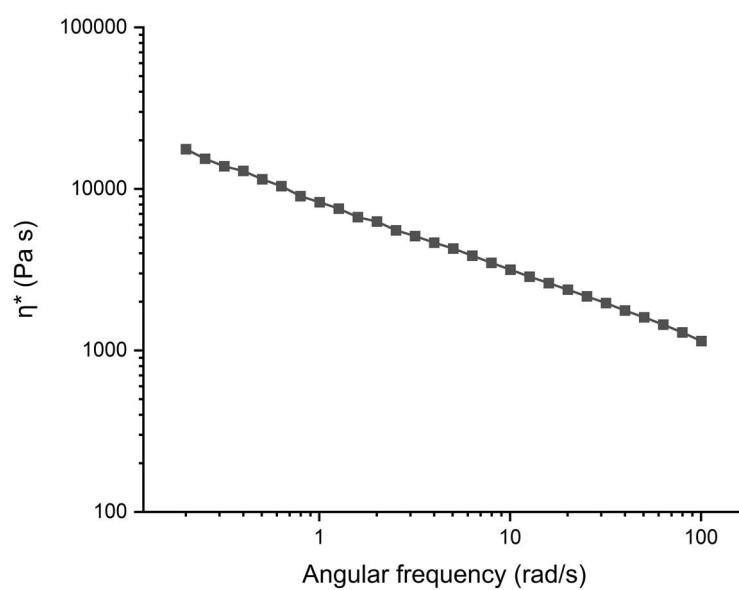


**Figure S39:** The amplitude sweep test (at 1 Hz, 190 °C) on **M8** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

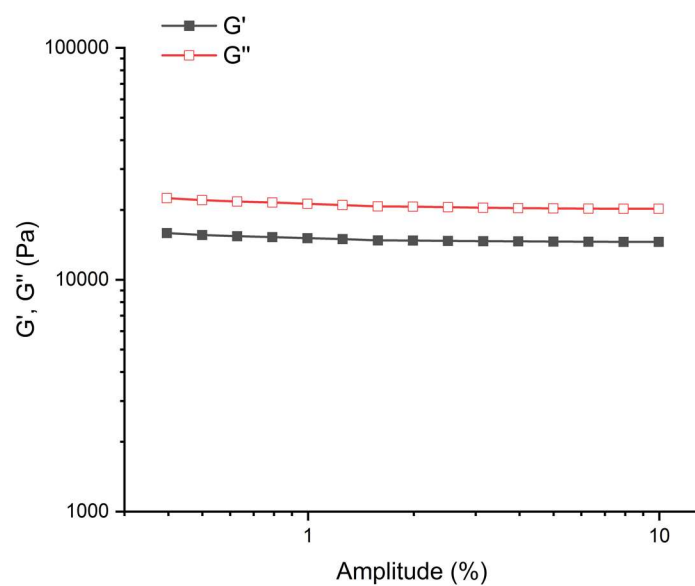
- **M9**



**Figure S40:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M9**.

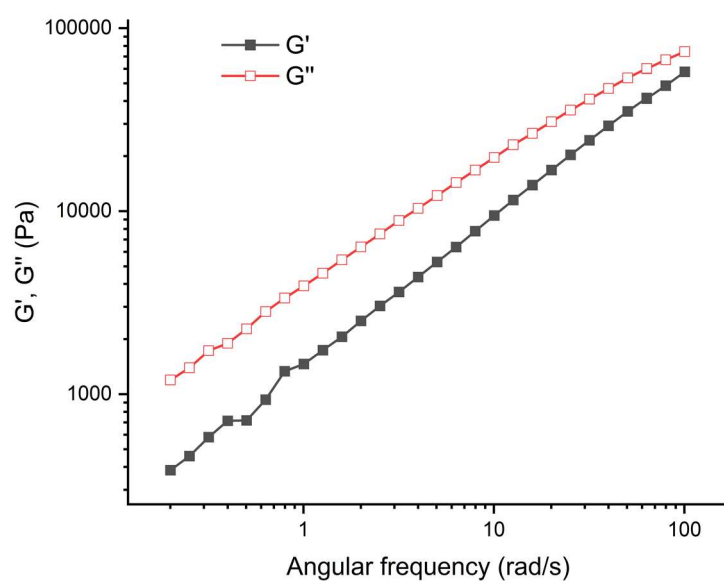


**Figure S41:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M9**.

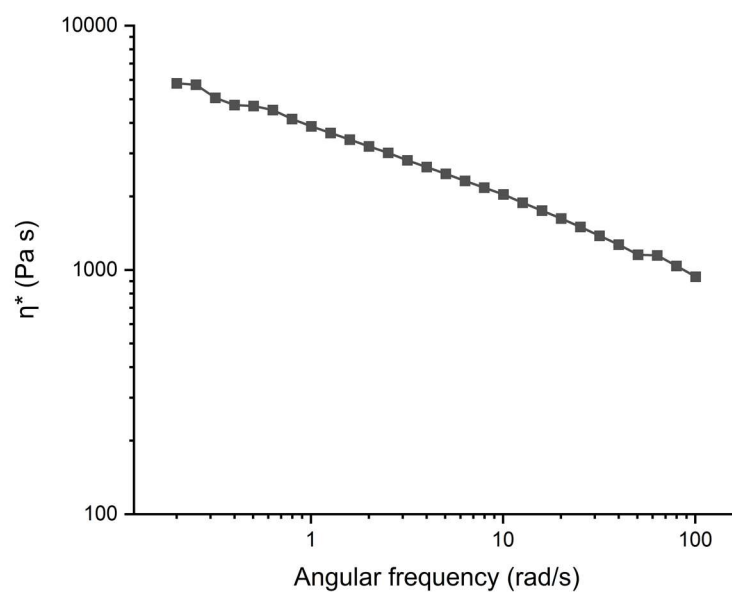


**Figure S42:** The amplitude sweep test (at 1 Hz, 190 °C) on **M9** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

- **M10**

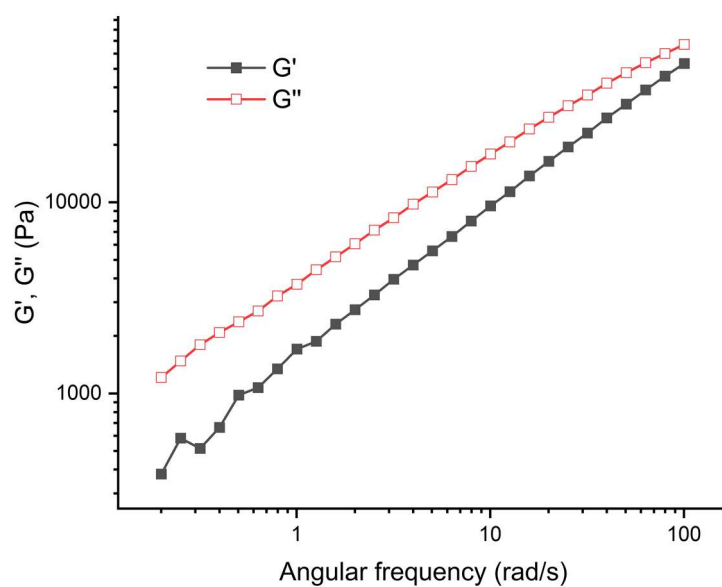


**Figure S43:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M10**.



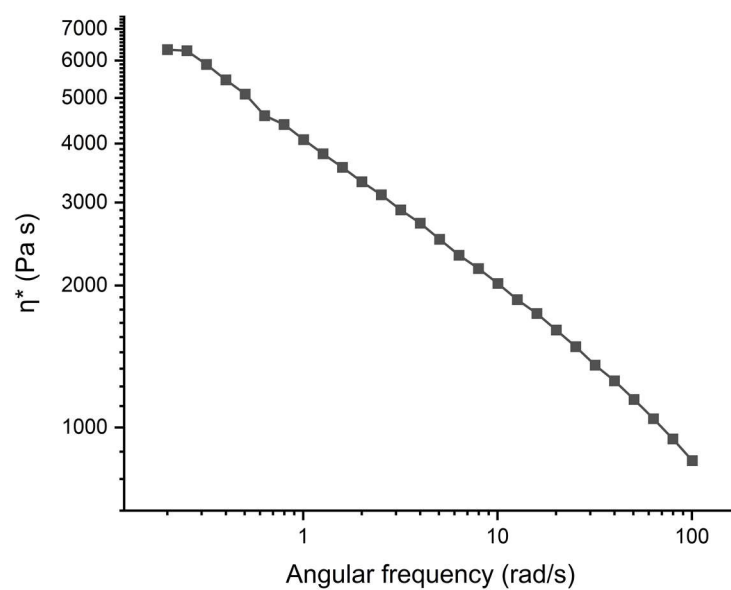
**Figure S44:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M10**.

- **M11**

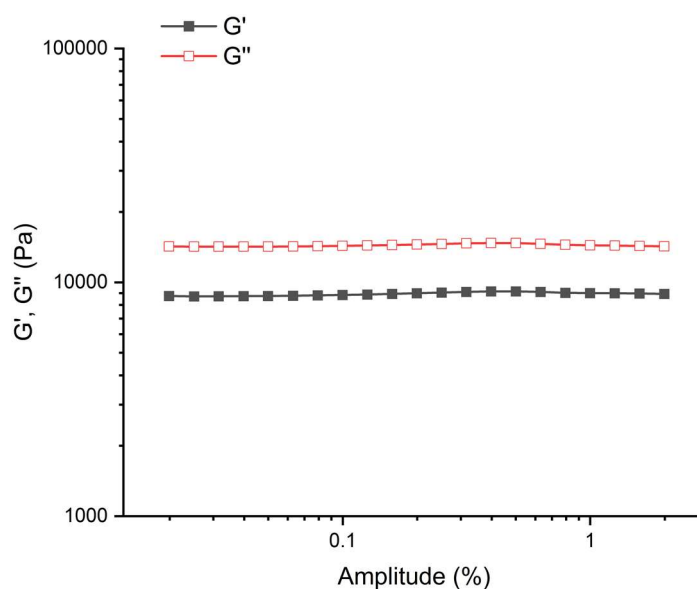


**Figure S45:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M11**.



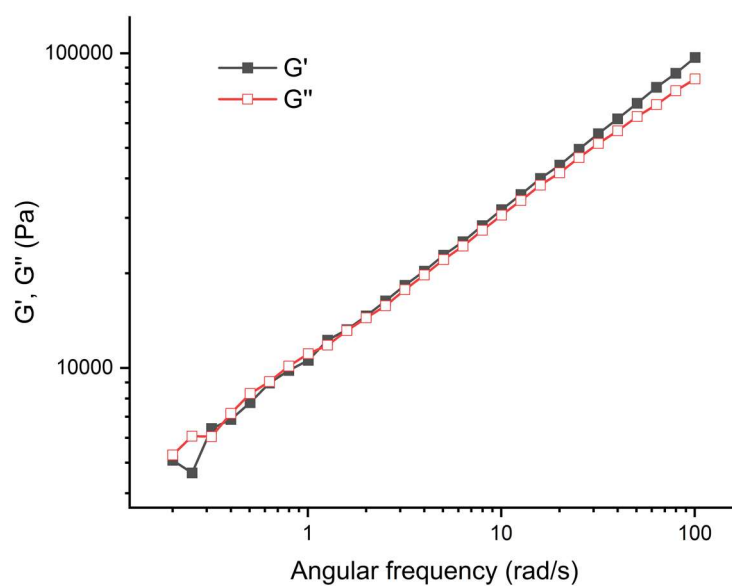


**Figure S46:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M11**.

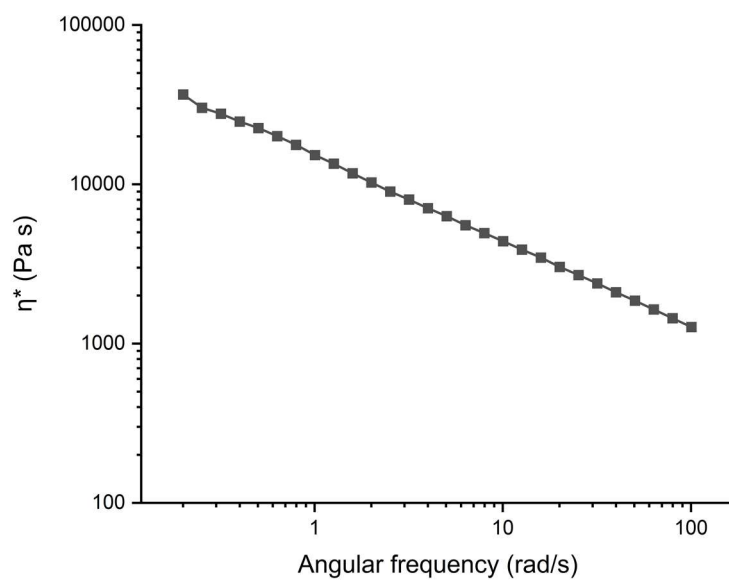


**Figure S47:** The amplitude sweep test (at 1 Hz, 190 °C) on **M11** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

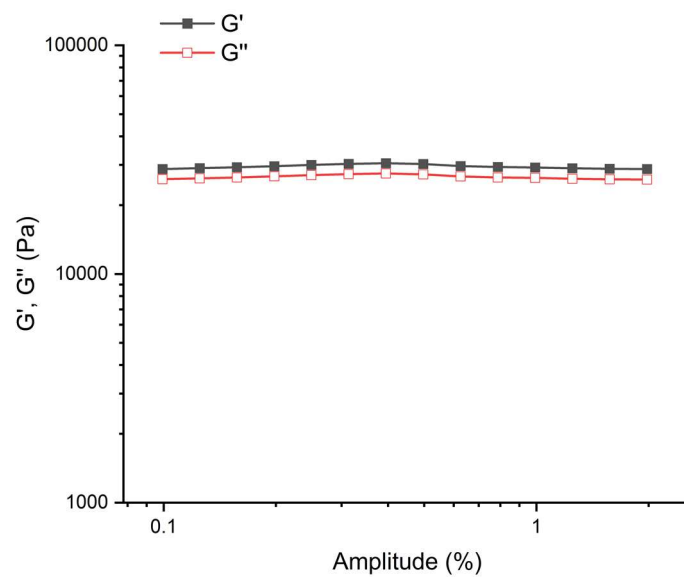
- **M12**



**Figure S48:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M12**.

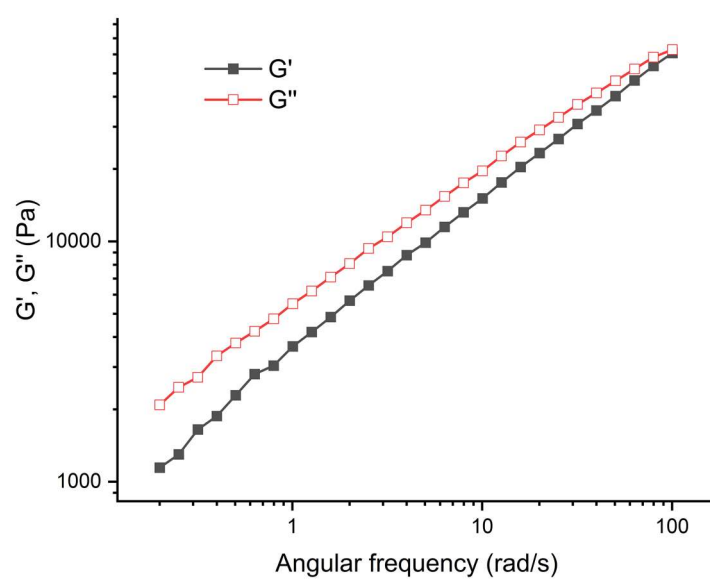


**Figure S49:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M12**.

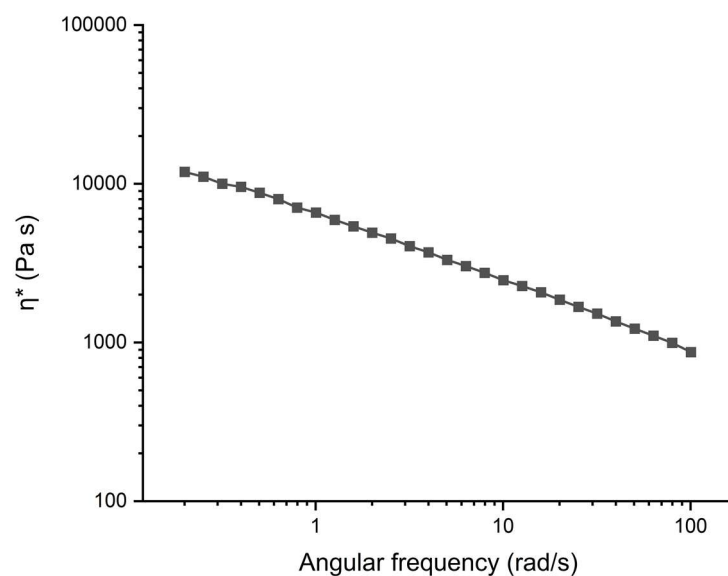


**Figure S50:** The amplitude sweep test (at 1 Hz, 190 °C) on **M12** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

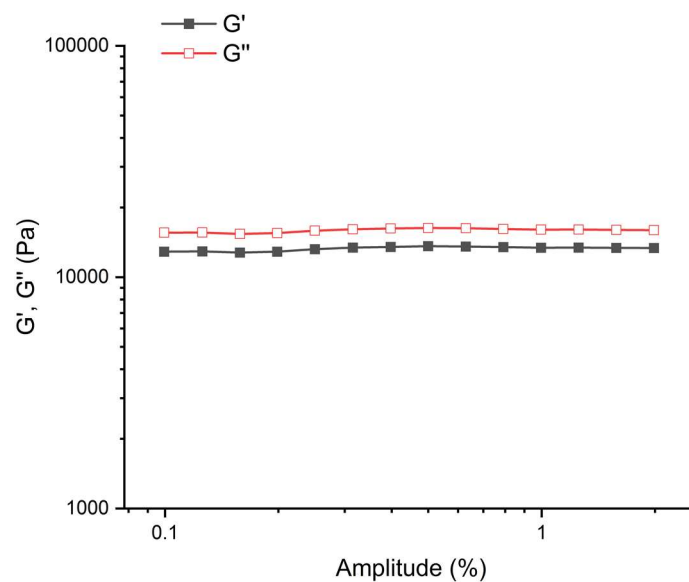
- **M13**



**Figure S51:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M13**.

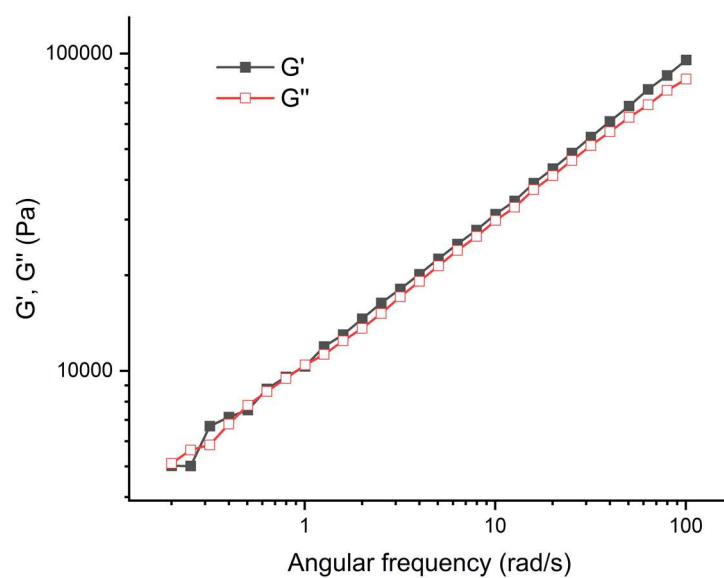


**Figure S52:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M13**.

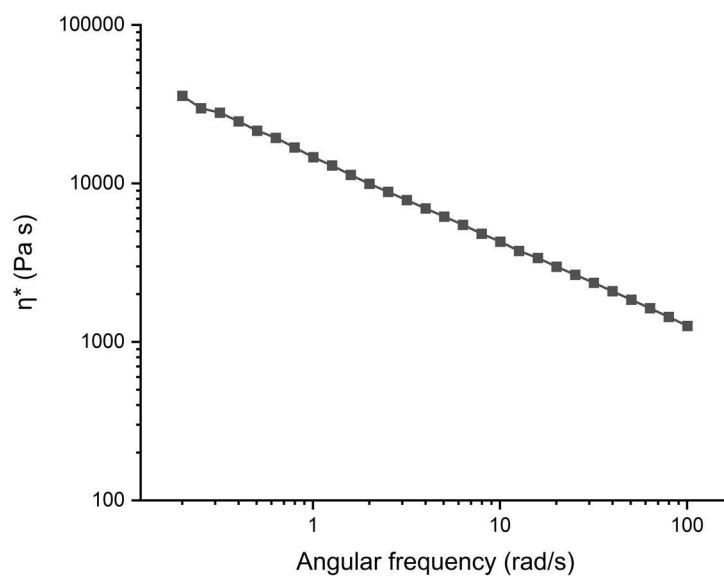


**Figure S53:** The amplitude sweep test (at 1 Hz, 190 °C) on **M13** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

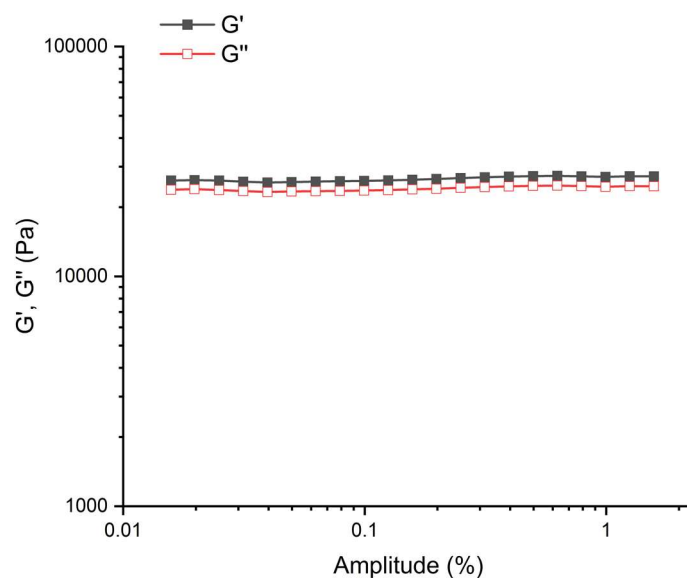
- **M14**



**Figure S54:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M14**.

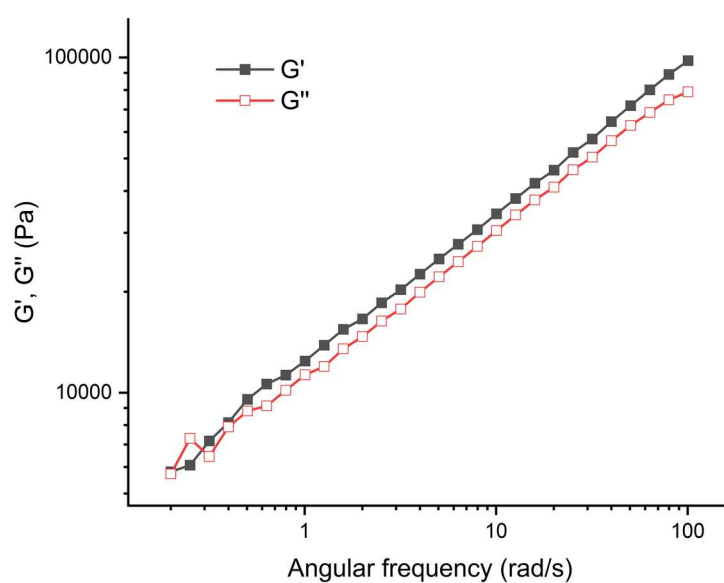


**Figure S55:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M14**.

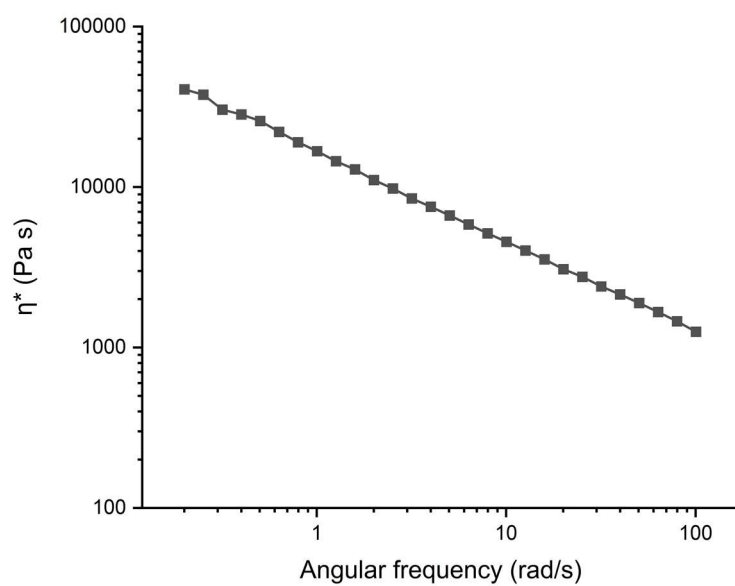


**Figure S56:** The amplitude sweep test (at 1 Hz, 190 °C) on **M14** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

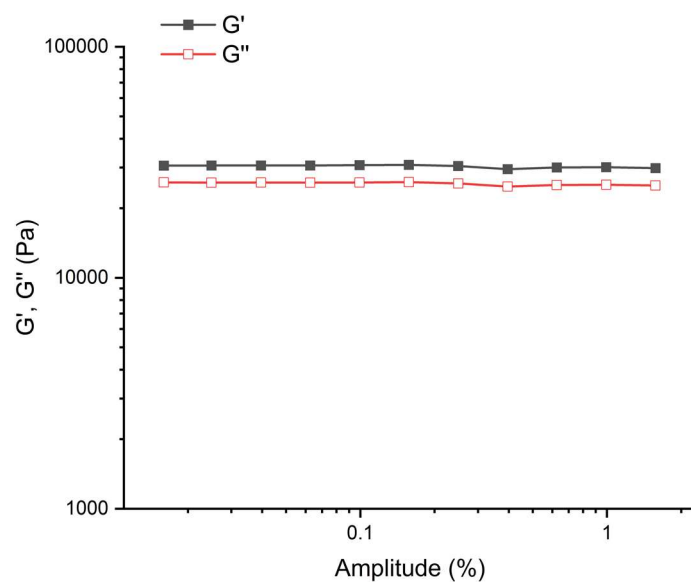
- **M15**



**Figure S57:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M15**.

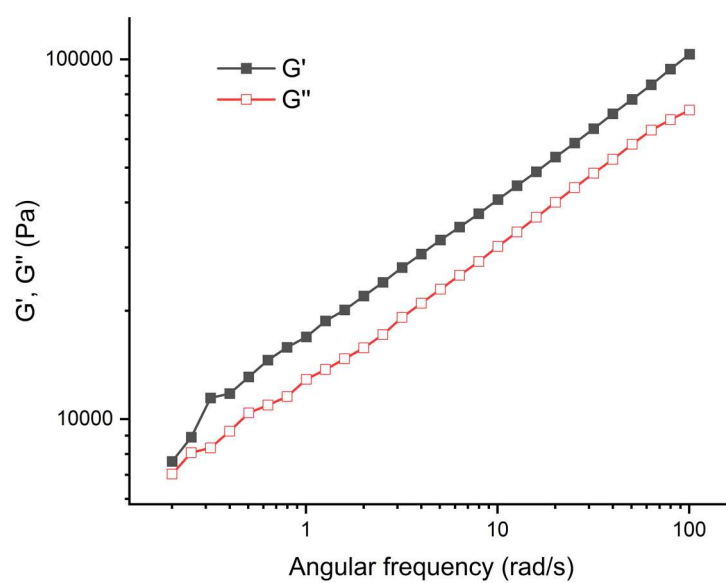


**Figure S58:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M15**.

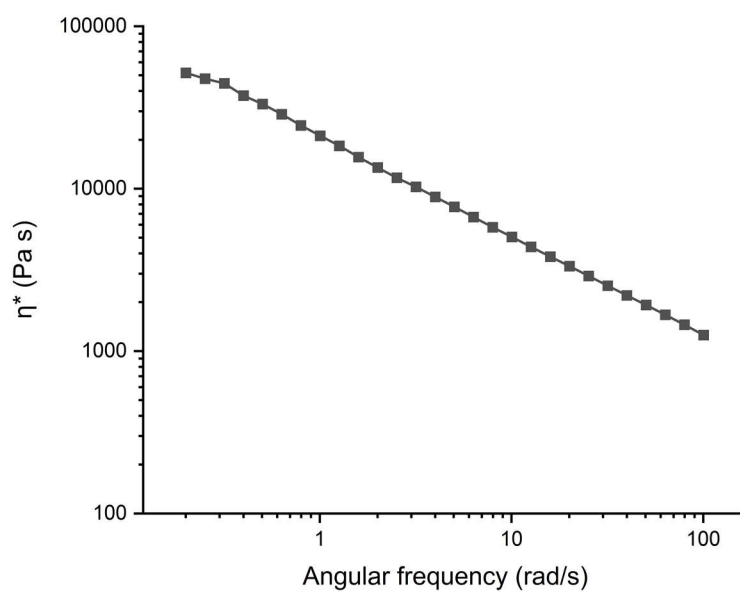


**Figure S59:** The amplitude sweep test (at 1 Hz, 190 °C) on **M15** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

- **M16**

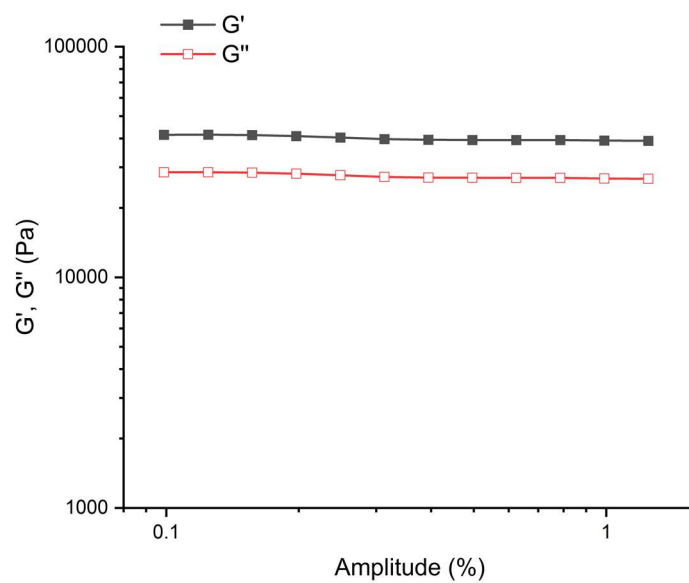


**Figure S60:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M16**.



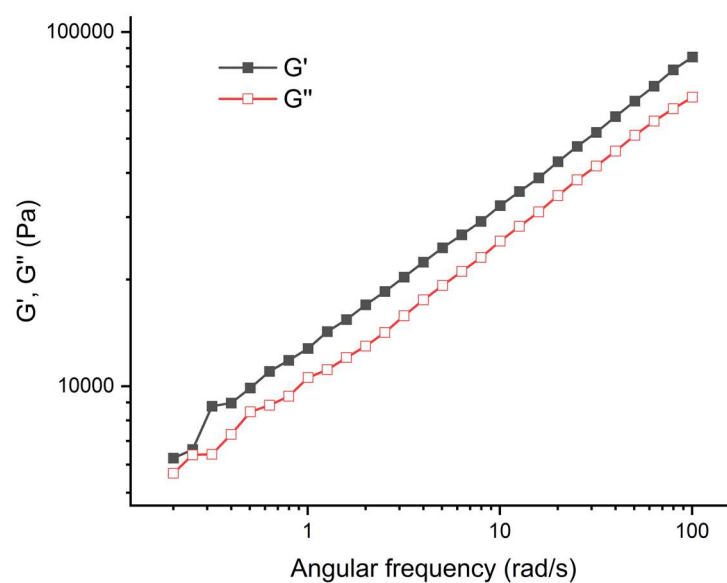
**Figure S61:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M16**.



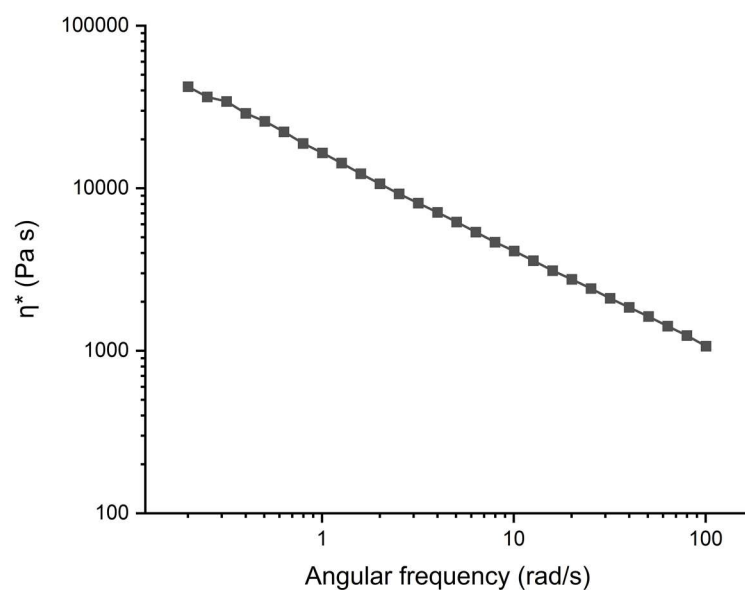


**Figure S62:** The amplitude sweep test (at 1 Hz, 190 °C) on **M16** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

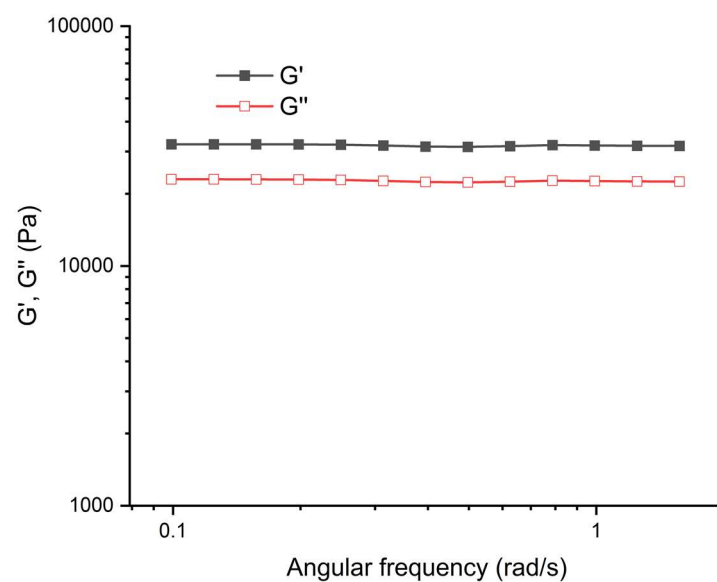
- **M17**



**Figure S63:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M17**.

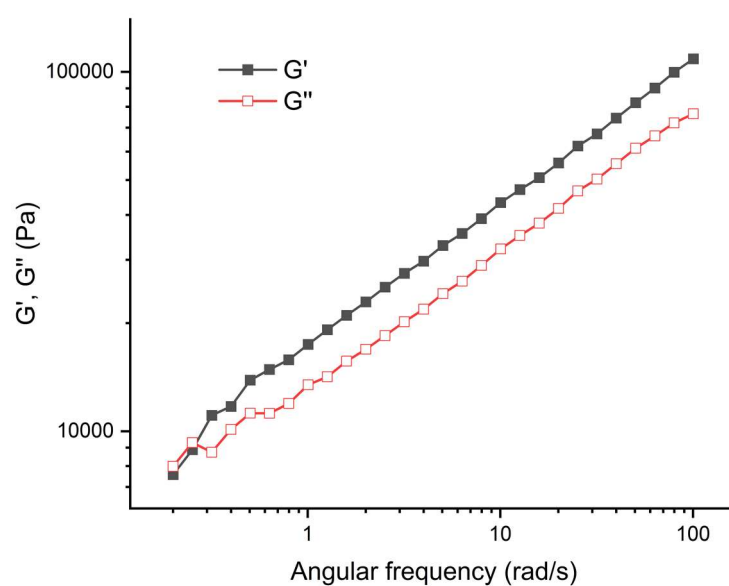


**Figure S64:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M17**.

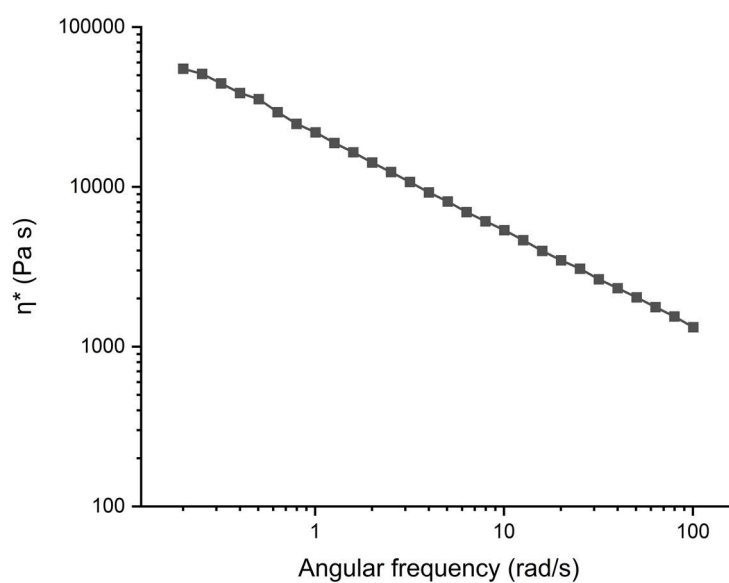


**Figure S65:** The amplitude sweep test (at 1 Hz, 190 °C) on **M17** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

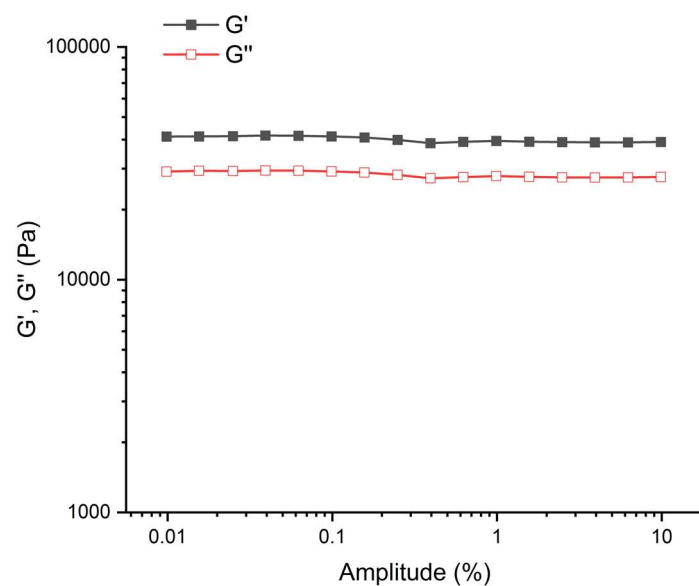
- **M18**



**Figure S66:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M18**.

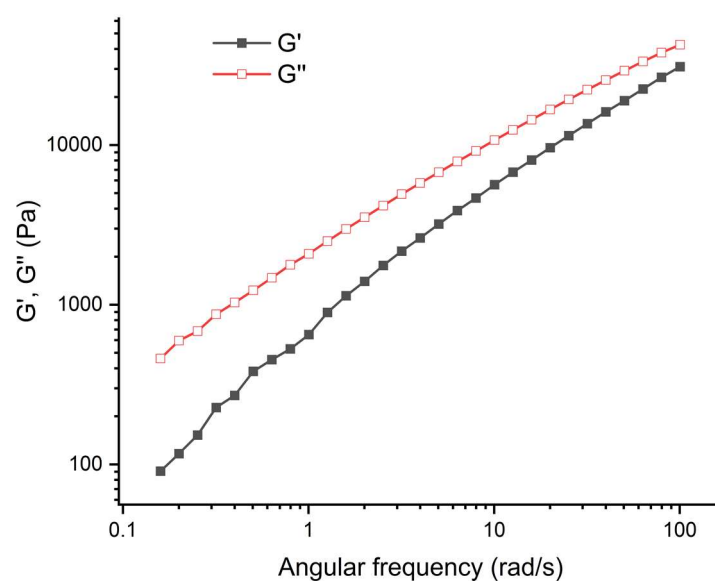


**Figure S67:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M18**.

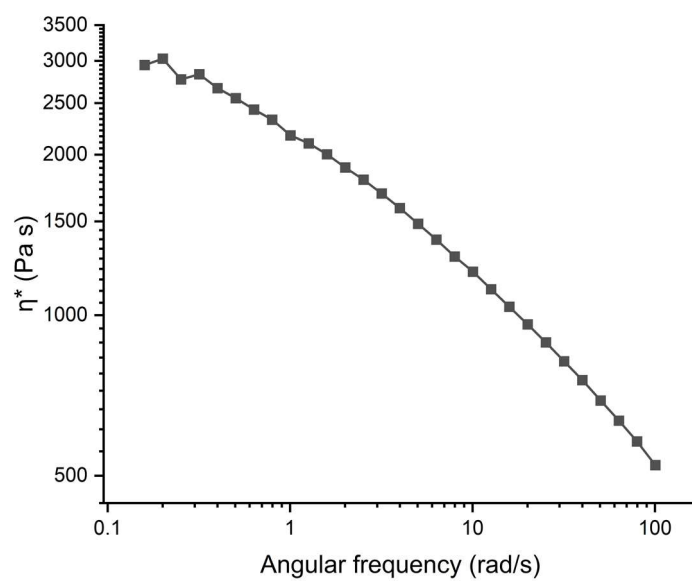


**Figure S68:** The amplitude sweep test (at 1 Hz, 190 °C) on **M18** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

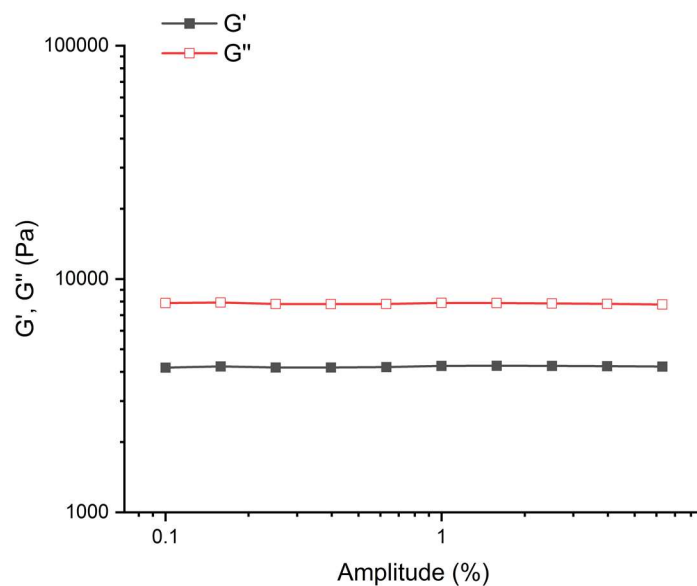
- **M19**



**Figure S69:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M19**.

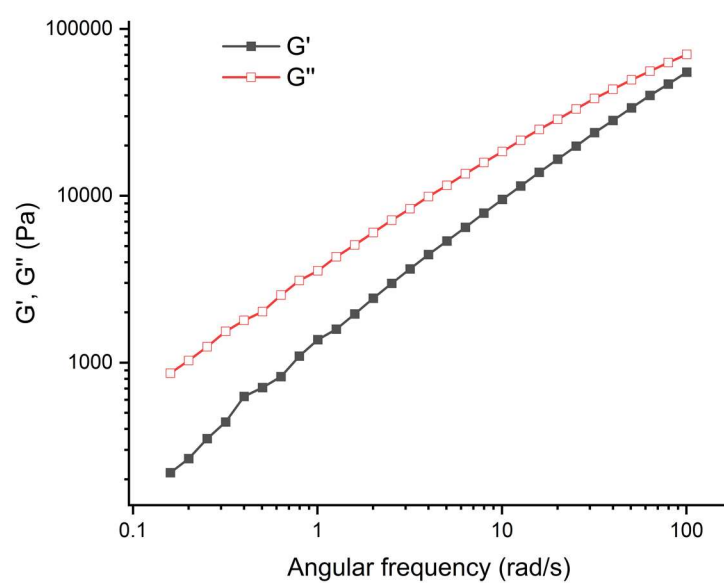


**Figure S70:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M19**.

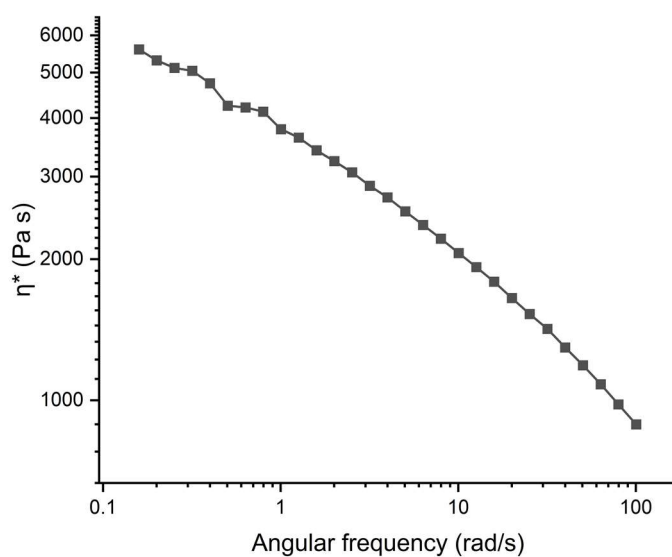


**Figure S71:** The amplitude sweep test (at 1 Hz, 190 °C) on **M19** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

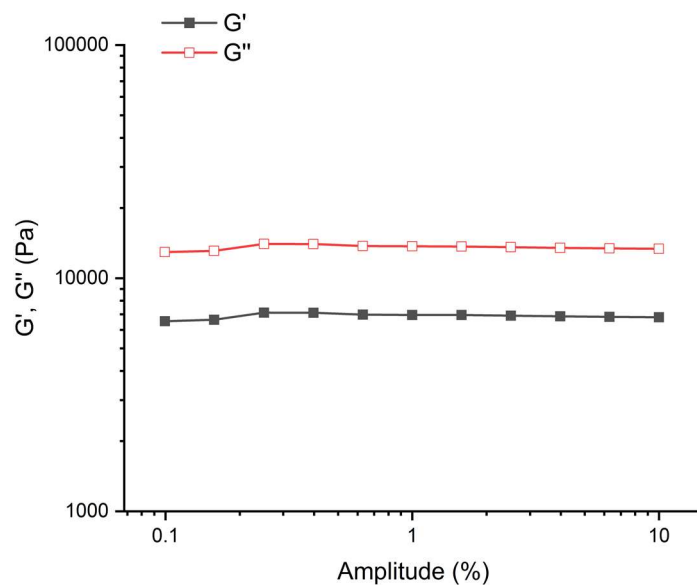
- **M20**



**Figure S72:** Frequency dependencies of the dynamic moduli (at 1% amplitude, 190 °C) for **M20**.

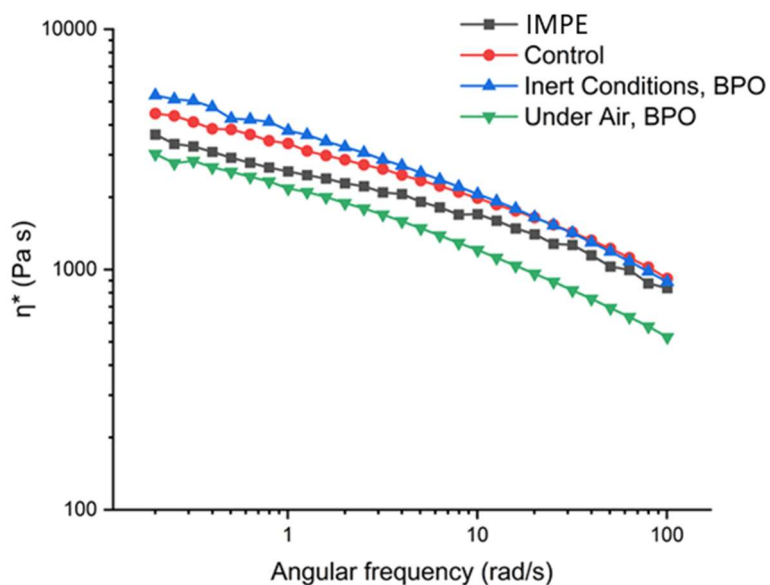


**Figure S73:** Frequency dependency of the complex viscosity (at 1% amplitude, 190 °C) for **M20**.



**Figure S74:** The amplitude sweep test (at 1 Hz, 190 °C) on **M20** showing how dynamic moduli behave as a function of amplitude, confirming the earlier frequency sweep measurement was performed at the LVER.

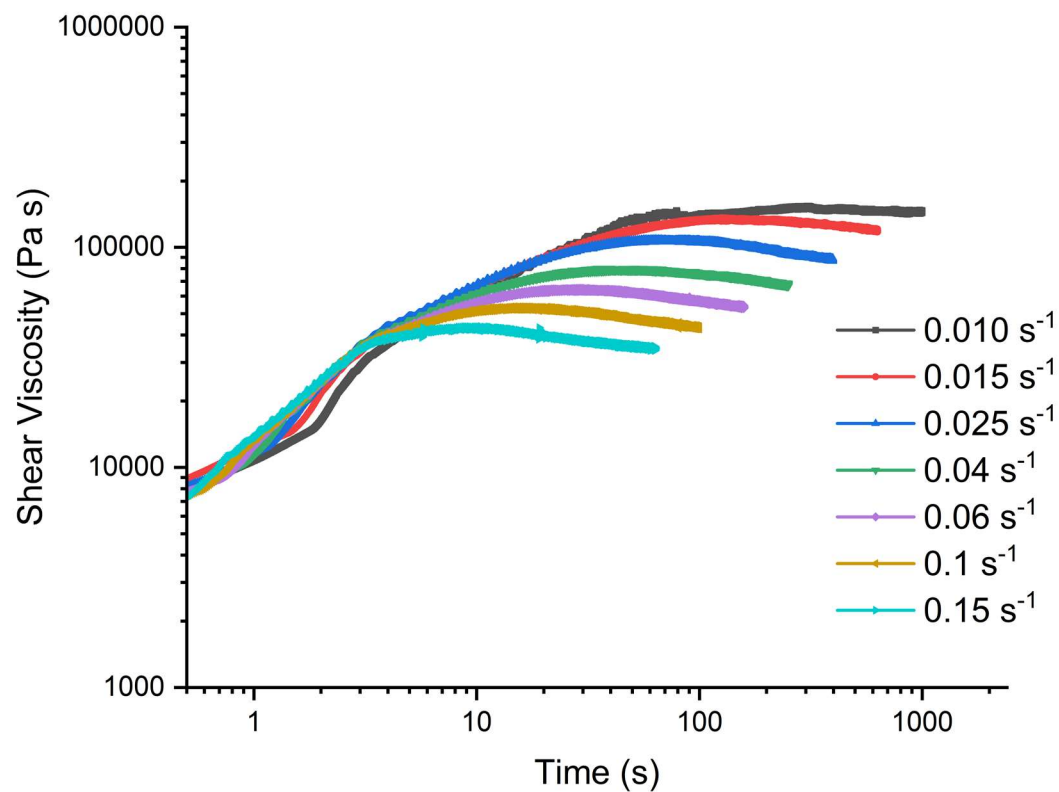
- **Comparison of IMPE, M1, M19 and M20**



**Figure S75:** Frequency dependencies of the complex viscosity values (at 1% amplitude, 190 °C) for **IMPE**, **M1**, **M19** and **M20**.

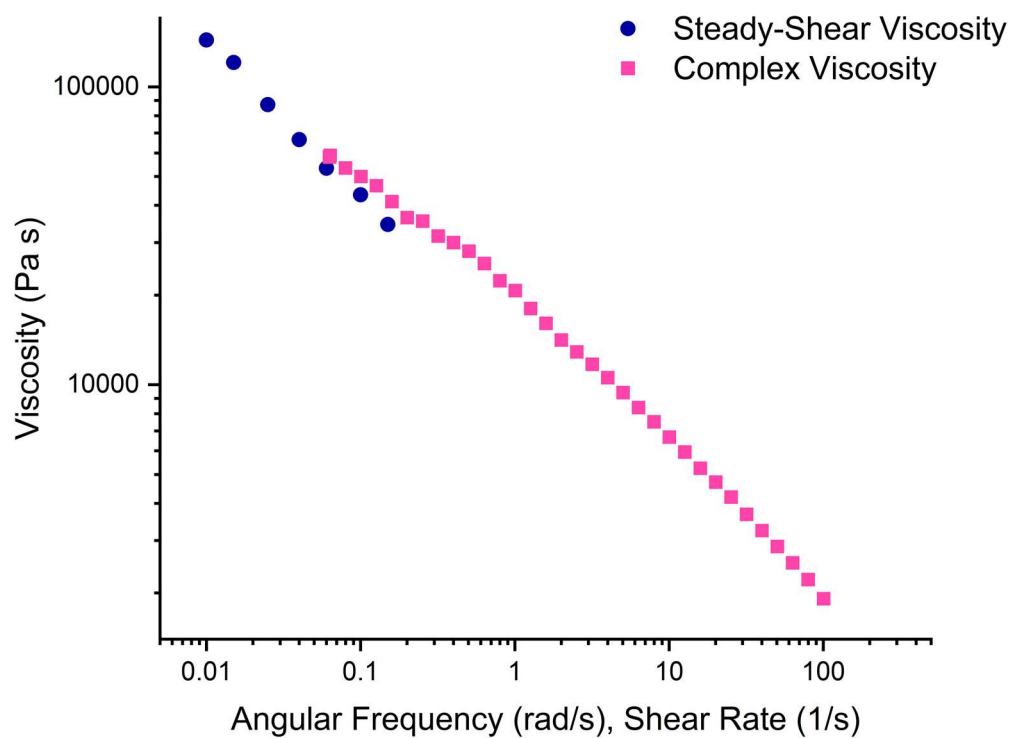
### 3 Nonlinear Rheology

- **BMPE**



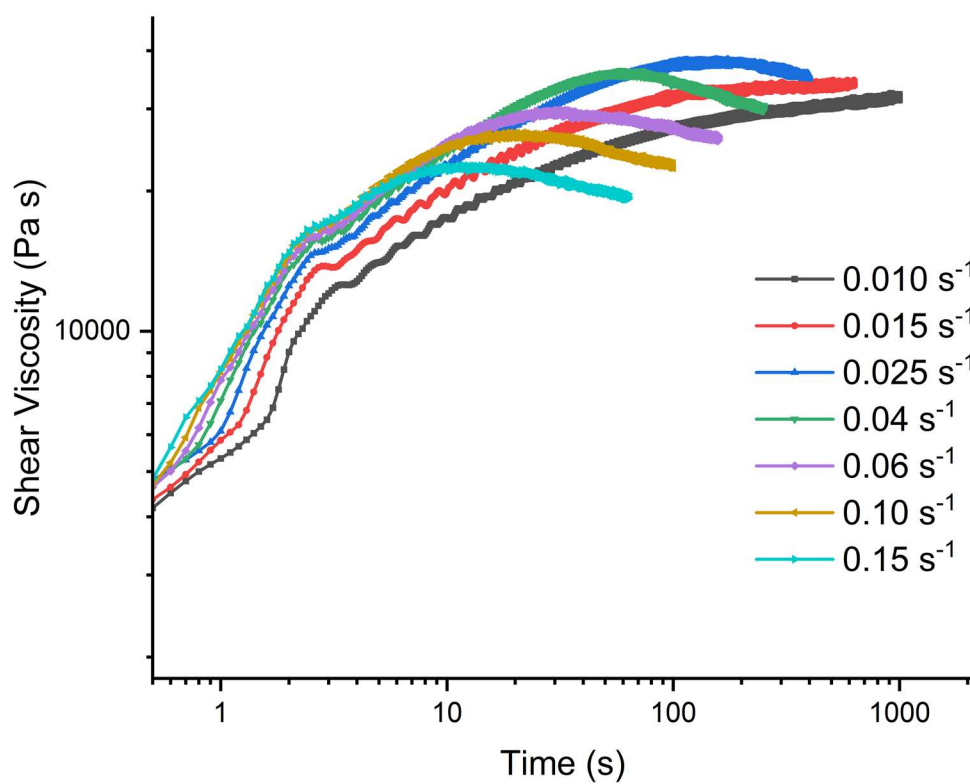
**Figure S76:** Step-shear non-linear rheology test on **BMPE** (at 190 °C) at different shear rates.



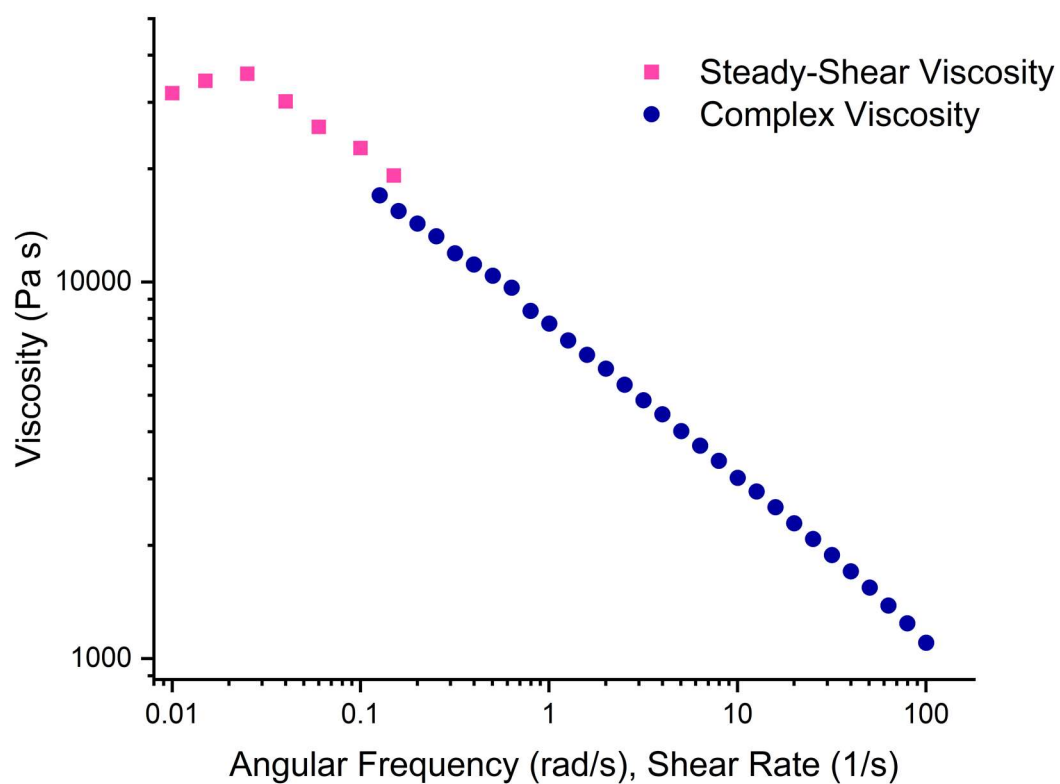


**Figure S77:** Dynamic viscosity (pink) and steady-state shear viscosity (blue) for **BMPE** to test the Cox-Merz rule.

- **M3**

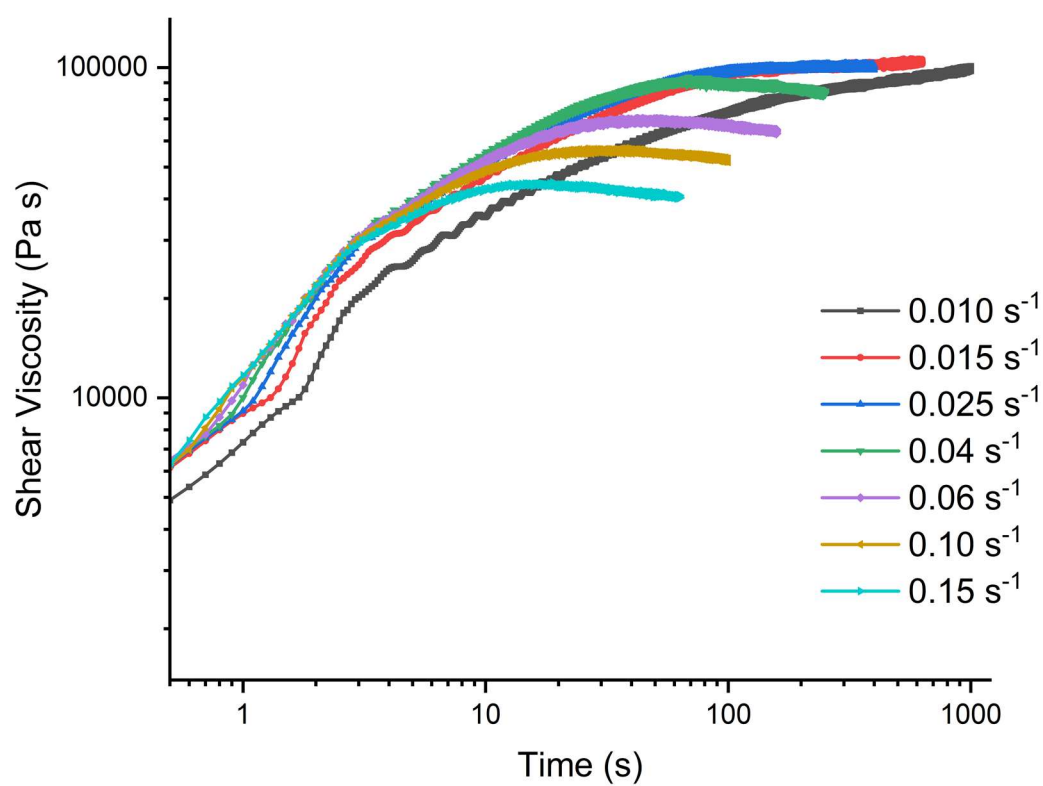


**Figure S78:** Step-shear non-linear rheology test on **M3** (at 190 °C) at different shear rates.

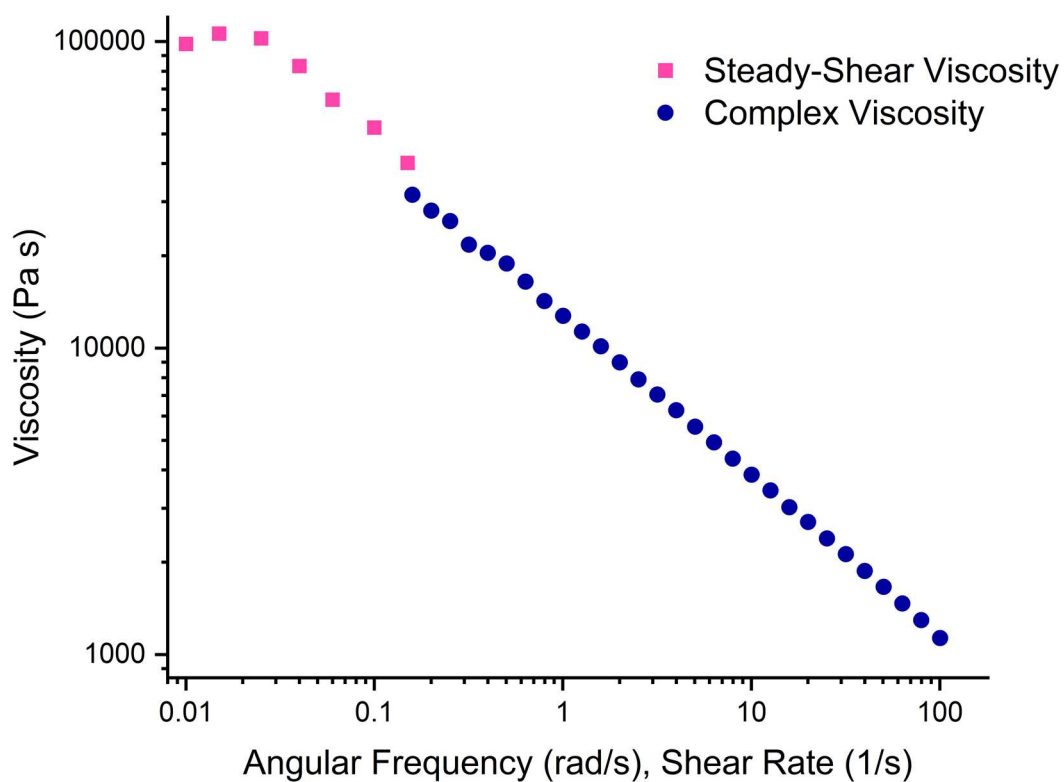


**Figure S79:** Dynamic viscosity (pink) and steady-state shear viscosity (blue) for **M3** to test the Cox-Merz rule.

- **M4**

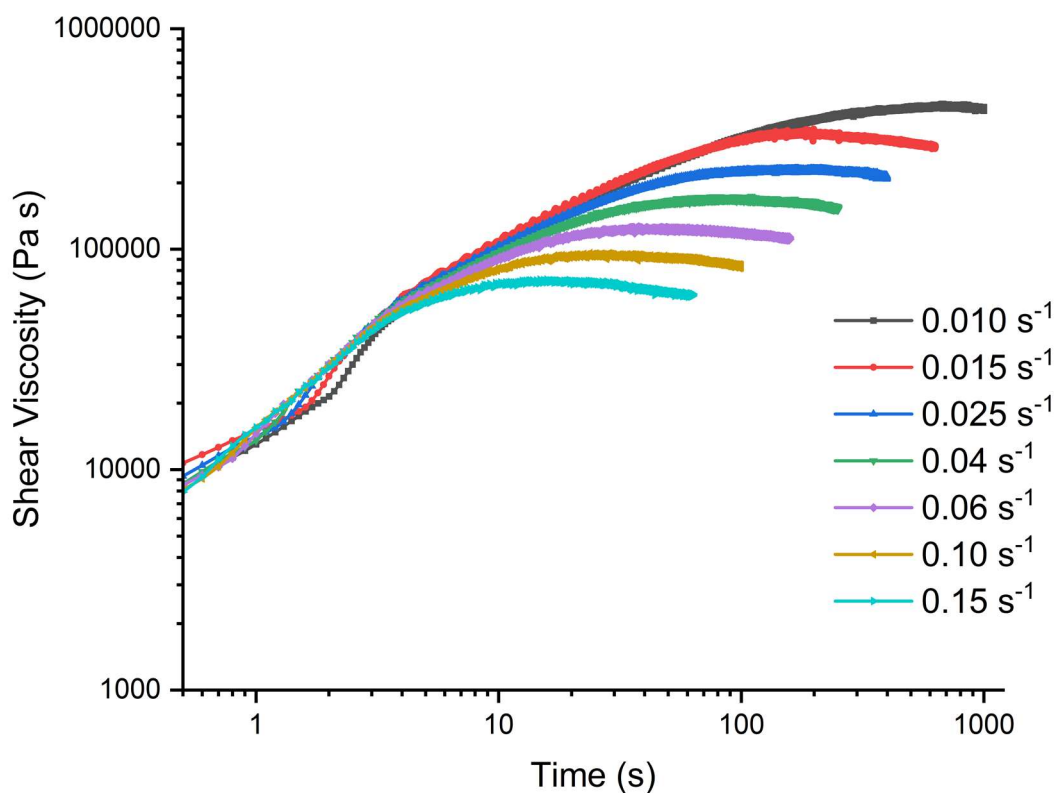


**Figure S80:** Step-shear non-linear rheology test on **M4** (at 190 °C) at different shear rates.

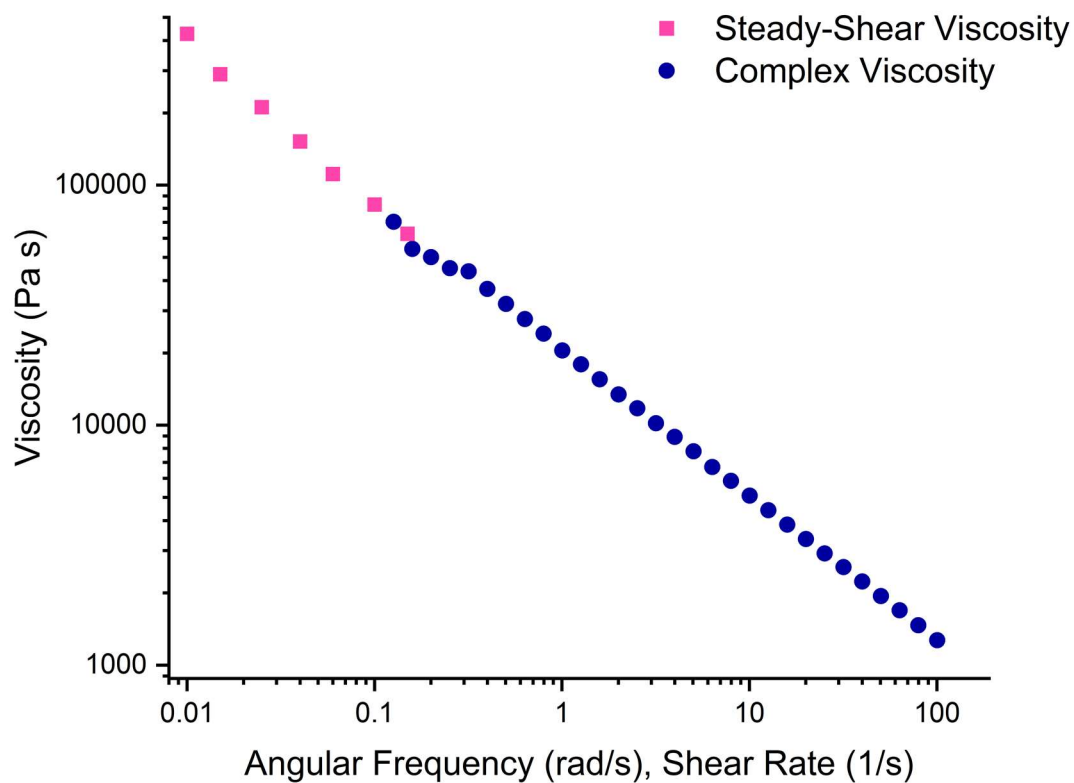


**Figure S81:** Dynamic viscosity (pink) and steady-state shear viscosity (blue) for **M4** to test the Cox-Merz rule.

- **M5**



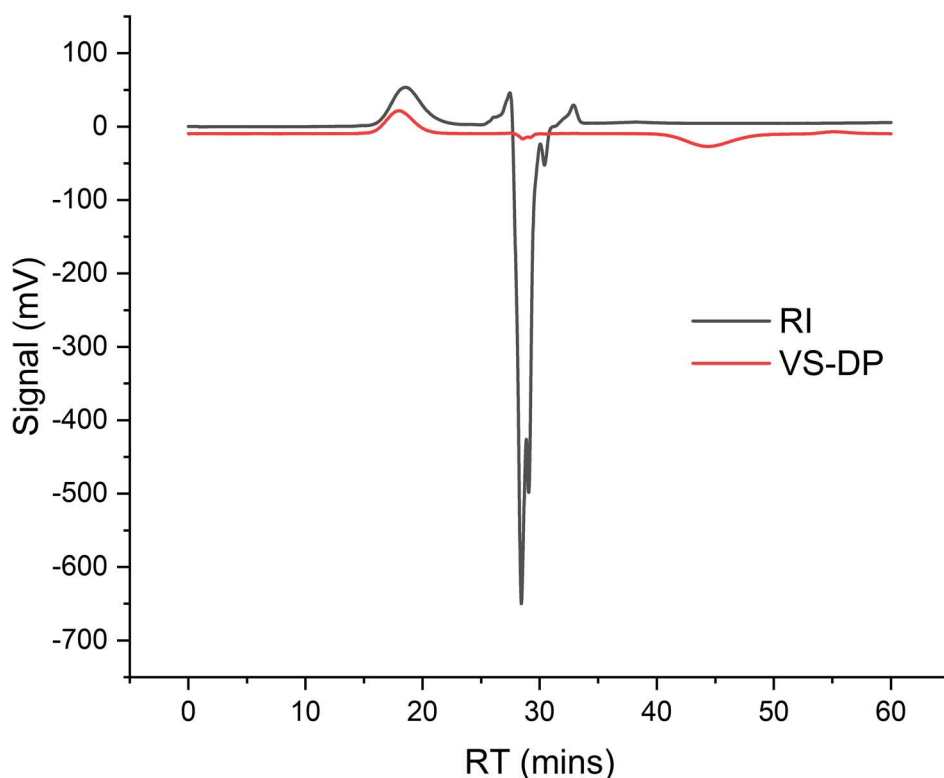
**Figure S82:** Step-shear non-linear rheology test on **M5** (at 190 °C) at different shear rates.



**Figure S83:** Dynamic viscosity (pink) and steady-state shear viscosity (blue) for **M5** to test the Cox-Merz rule.

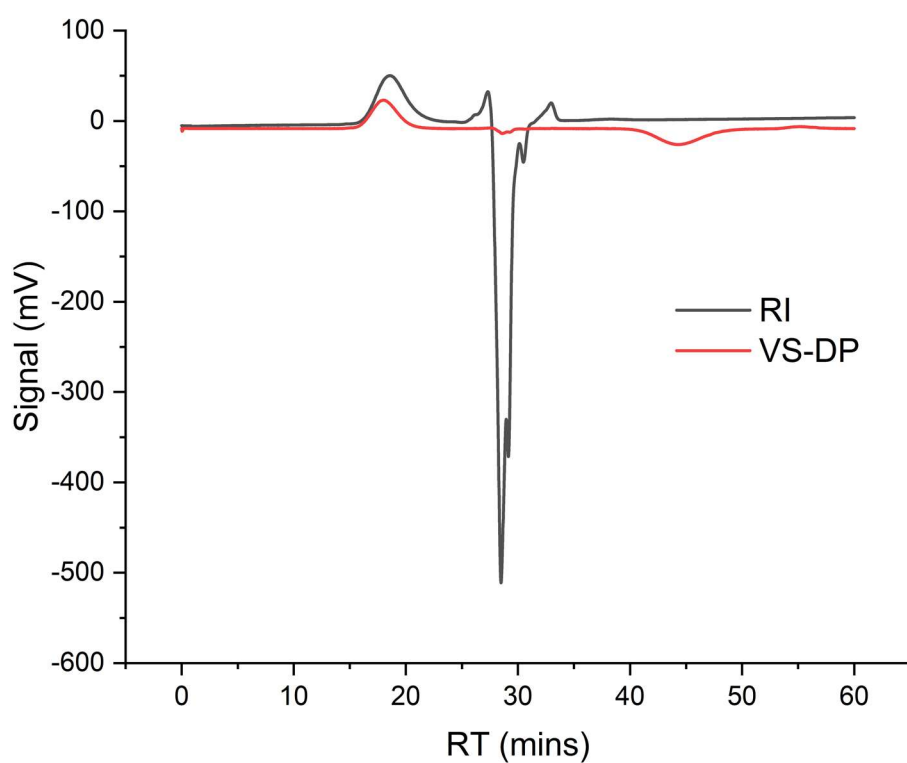
## 4 Size Exclusion Chromatograms of the Modified Samples

### • M1



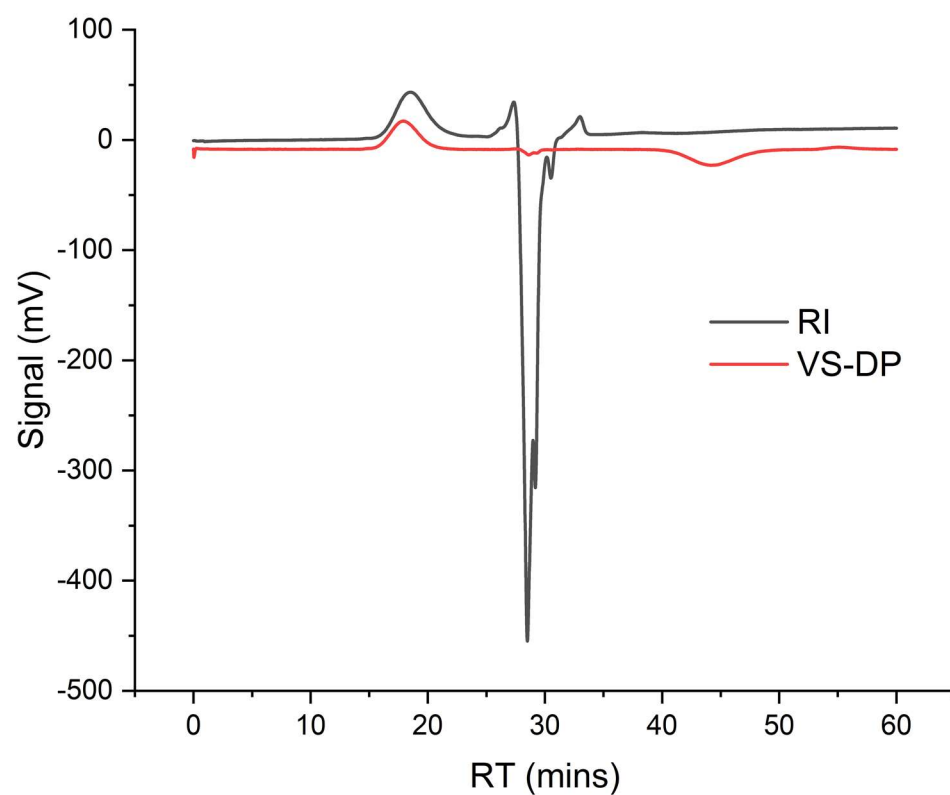
**Figure S84:** Raw GPC refractive index (RI) and viscometer differential pressure (VS-DP) traces recorded over retention time (RT) for **M1**.

- **M2**



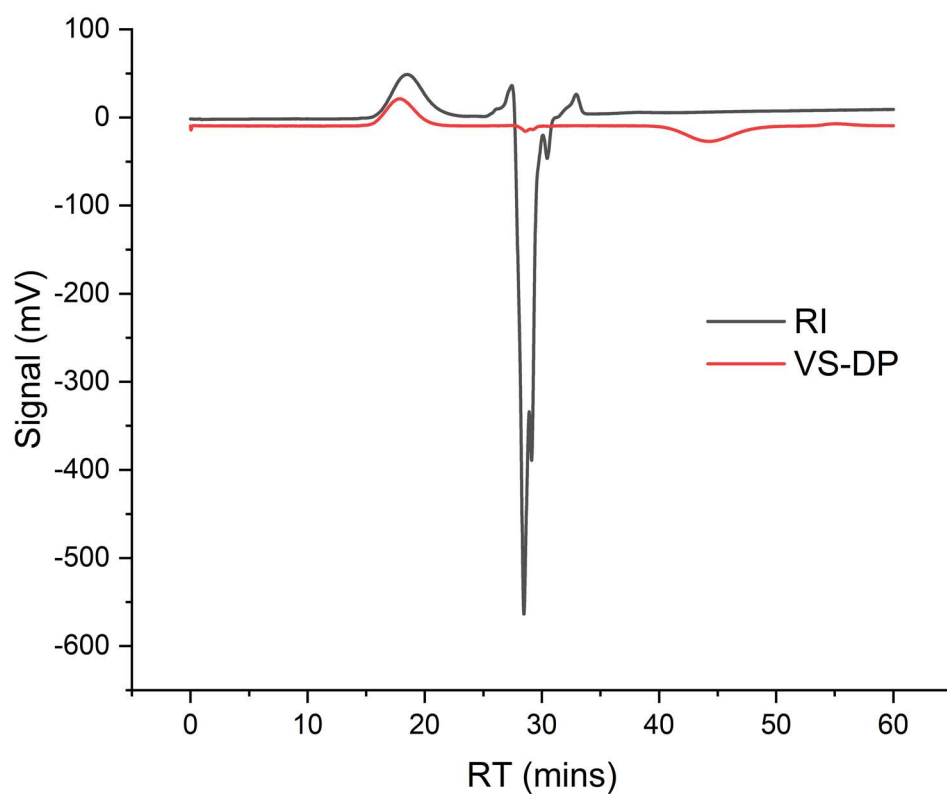
**Figure S85:** Raw GPC RI and VS-DP traces recorded over RT for **M2**.

- **M3**



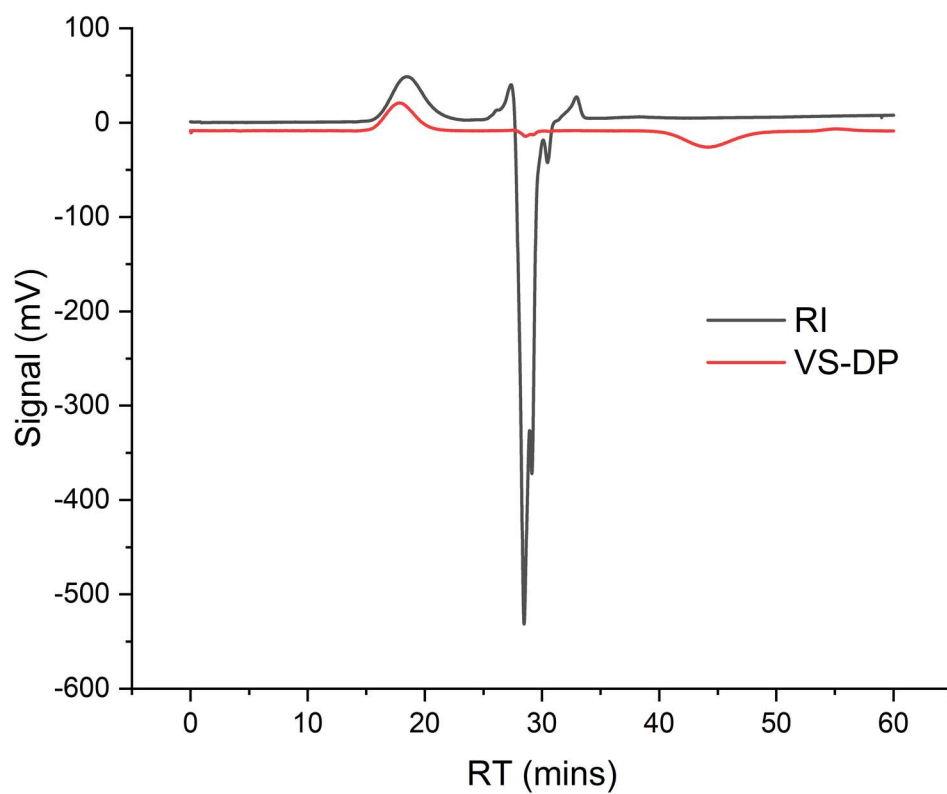
**Figure S86:** Raw GPC RI and VS-DP traces recorded over RT for **M3**.

- **M4**



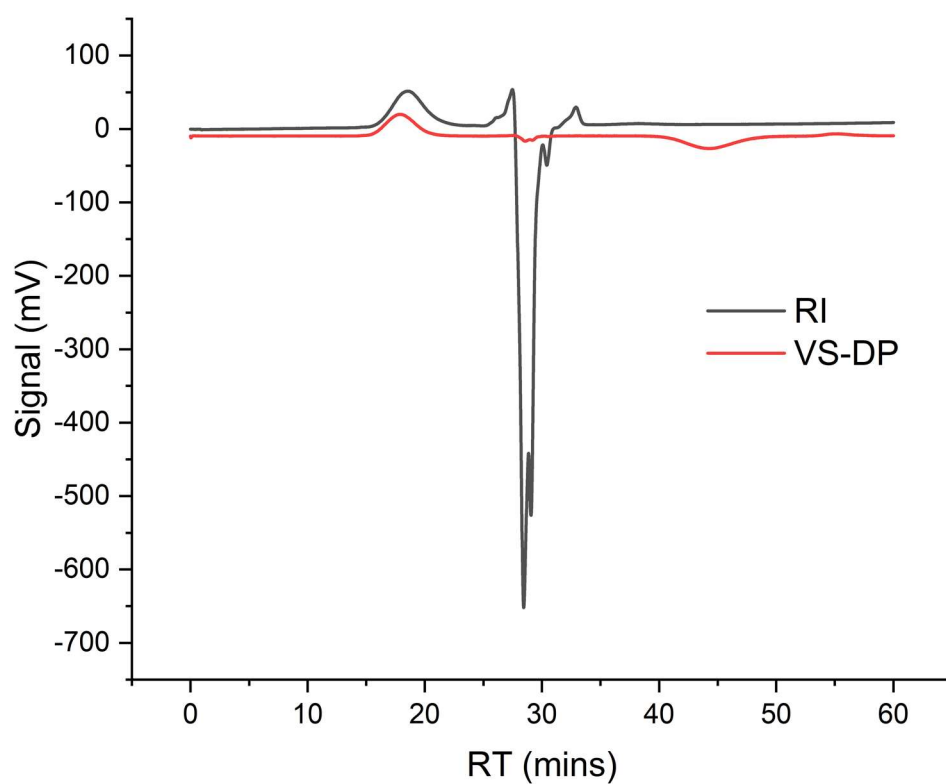
**Figure S87:** Raw GPC RI and VS-DP traces recorded over RT for **M4**.

- **M5**



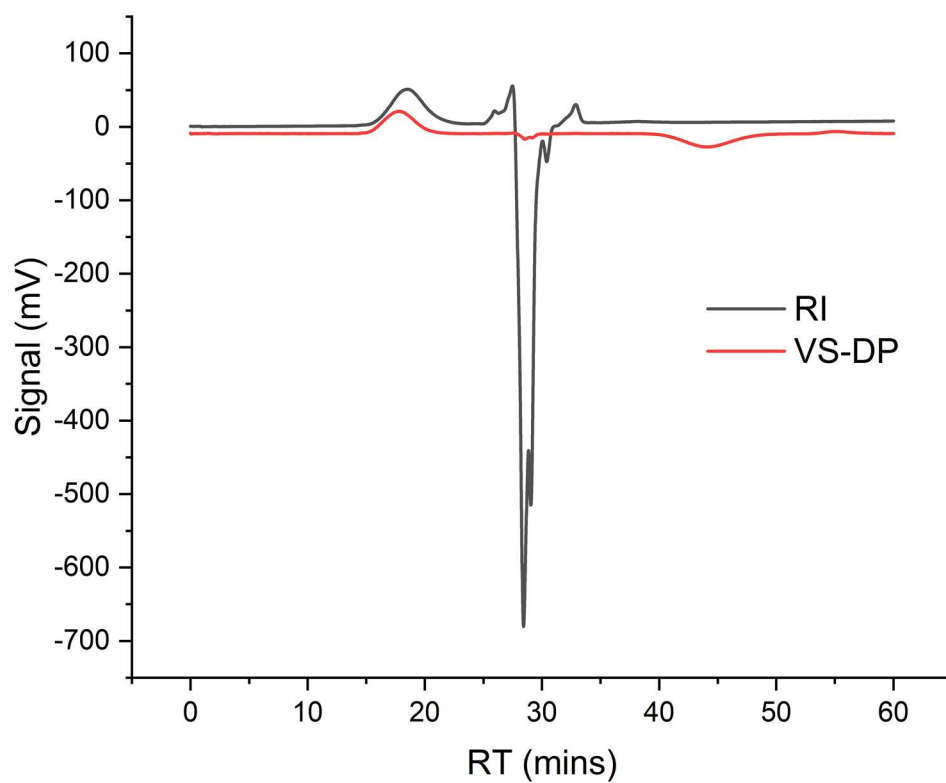
**Figure S88:** Raw GPC RI and VS-DP traces recorded over RT for **M5**.

- **M15**



**Figure S89:** Raw GPC RI and VS-DP traces recorded over RT for **M15**.

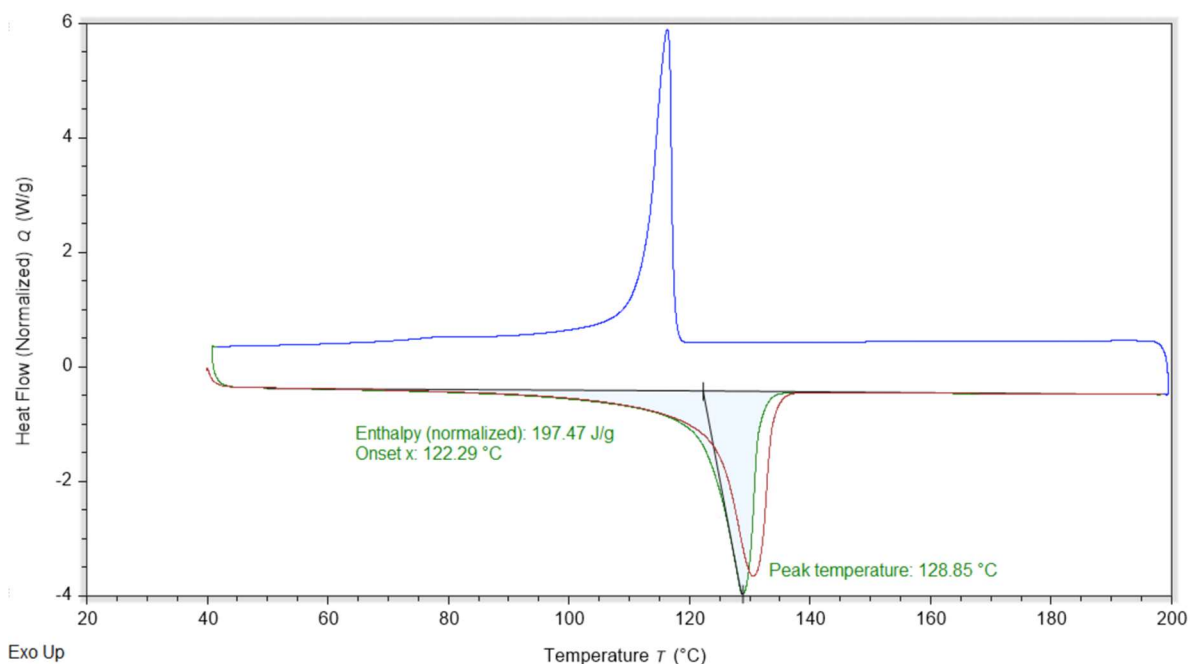
- **M16**



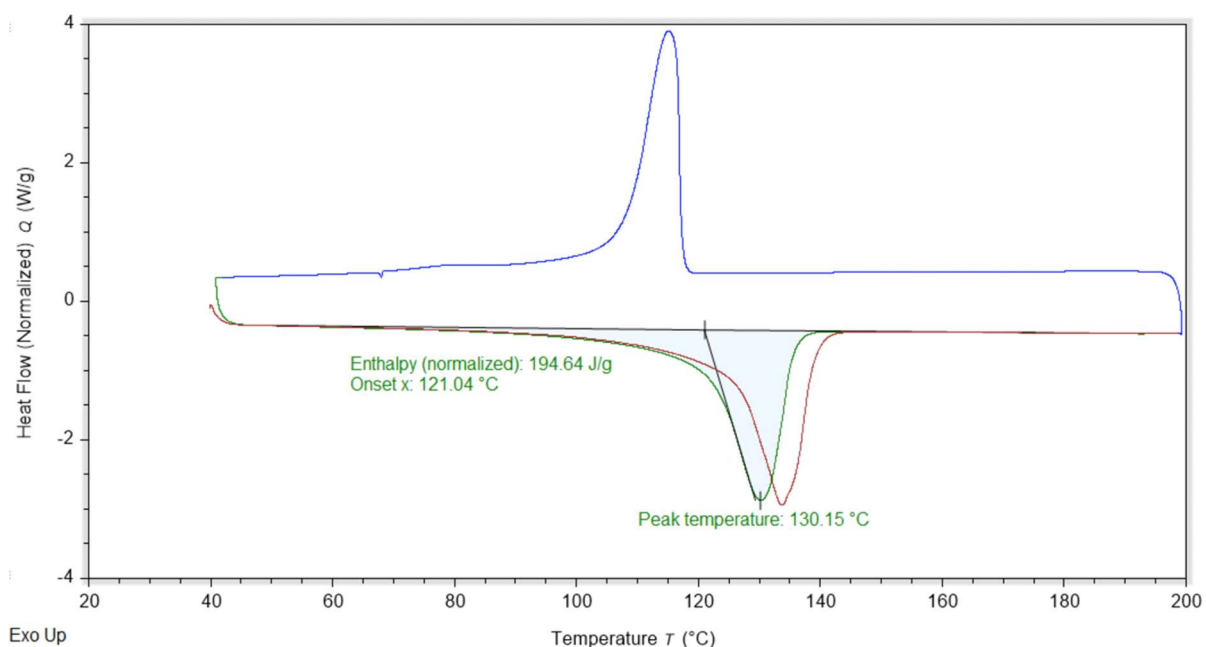
**Figure S90:** Raw GPC RI and VS-DP traces recorded over RT for **M16**.

## 5 Differential Scanning Calorimetry (DSC) Results of the Modified Samples

### • M1

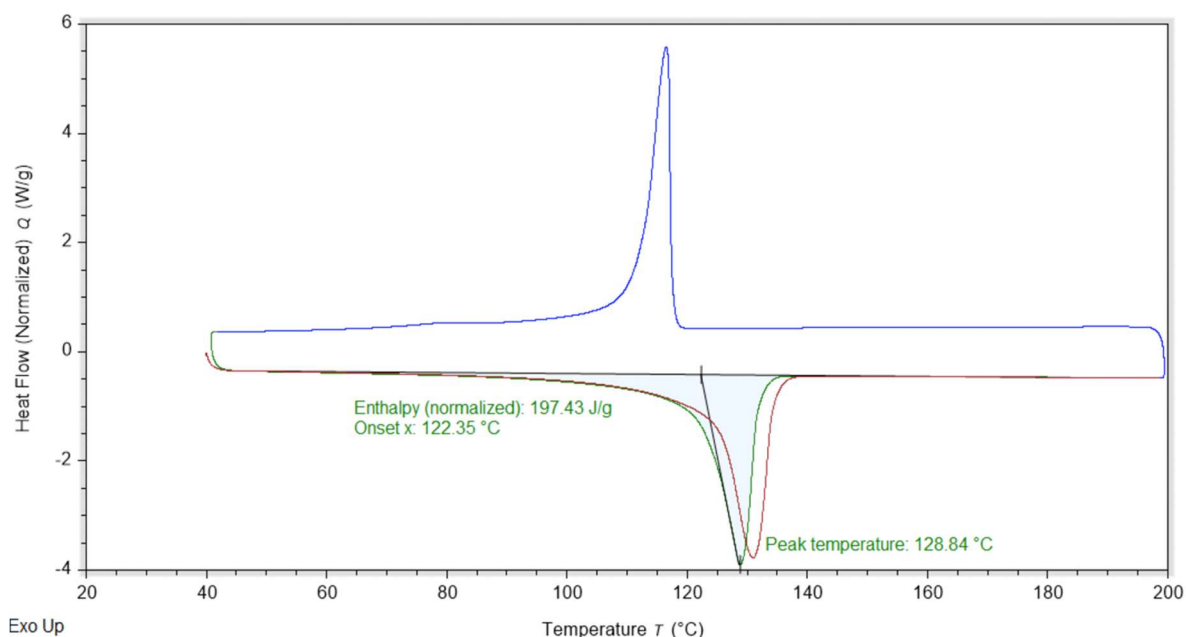


**Figure S91:** Heat flow traces recorded during the first test of **M1** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.



**Figure S92:** Heat flow traces recorded during the second test of **M1** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.





**Figure S93:** Heat flow traces recorded during the third test of **M1** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

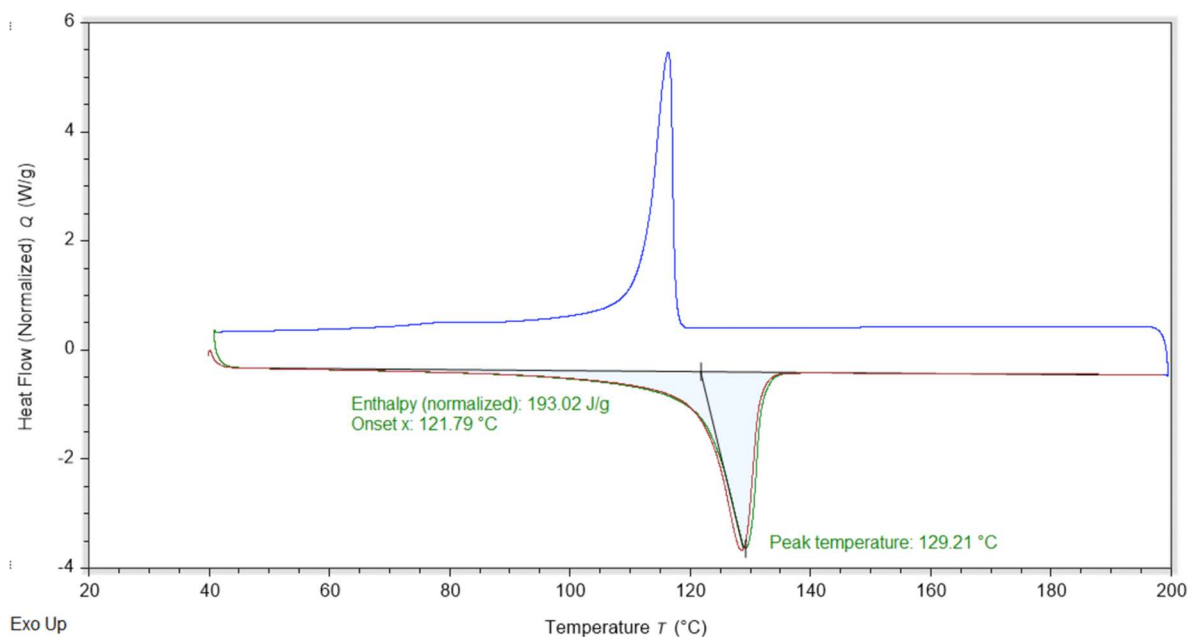
**Calculation S2:** An example calculation of the polymer sample crystallinity using the energy changes observed with **M1**.

$$\text{Average energy change} = (197.47 \text{ J/g} + 194.64 \text{ J/g} + 197.43 \text{ J/g}) / 3 = 196.51 \text{ J/g}$$

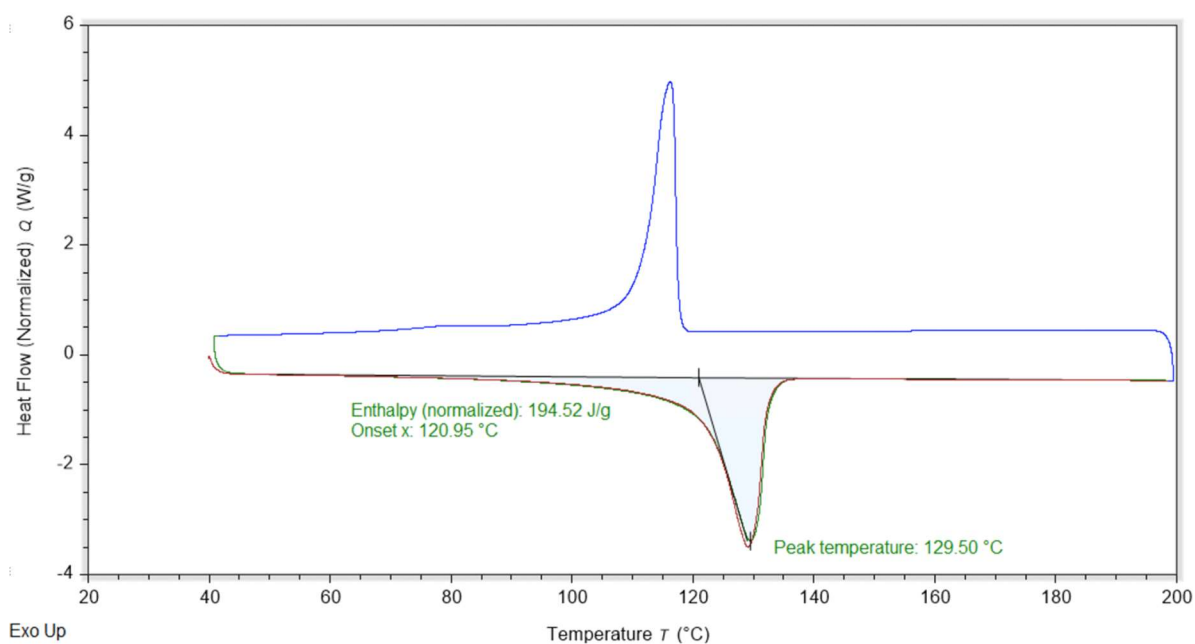
$$\text{Predicted energy change in a 100\% crystalline HDPE sample} = 290 \text{ J/g}$$

$$\% \text{Crystallinity of } \mathbf{M1} = ((196.51 \text{ J/g}) / (290 \text{ J/g})) * 100 = 67.8\%$$

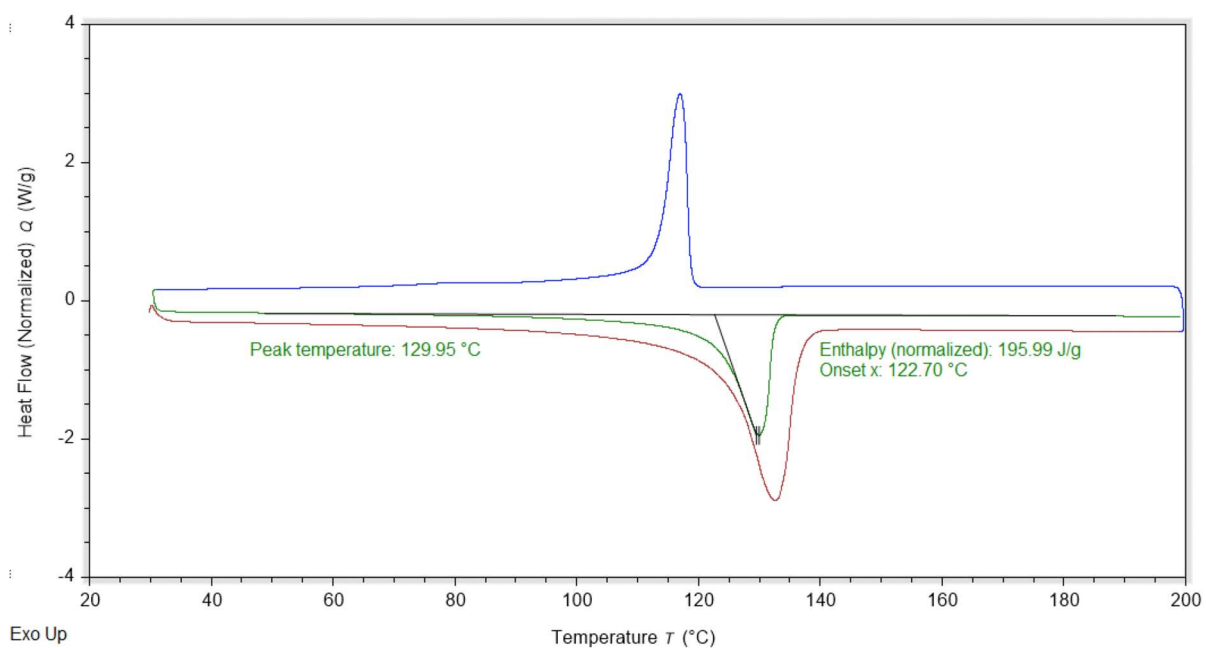
## • **M2**



**Figure S94:** Heat flow traces recorded during the first test of **M2** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

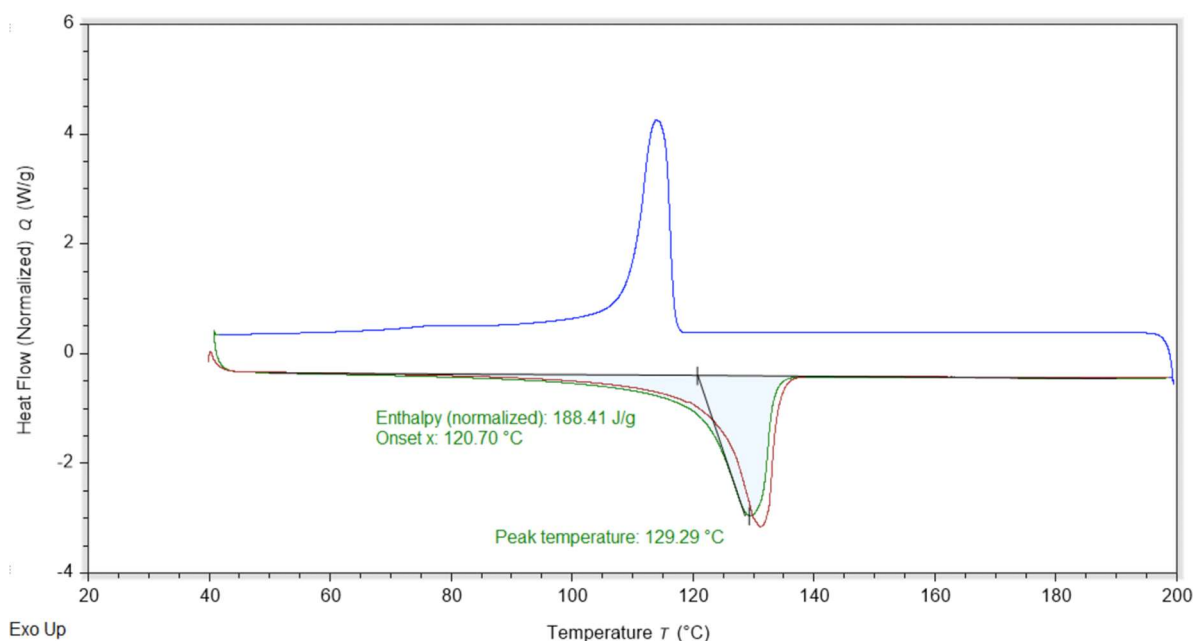


**Figure S95:** Heat flow traces recorded during the second test of **M2** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

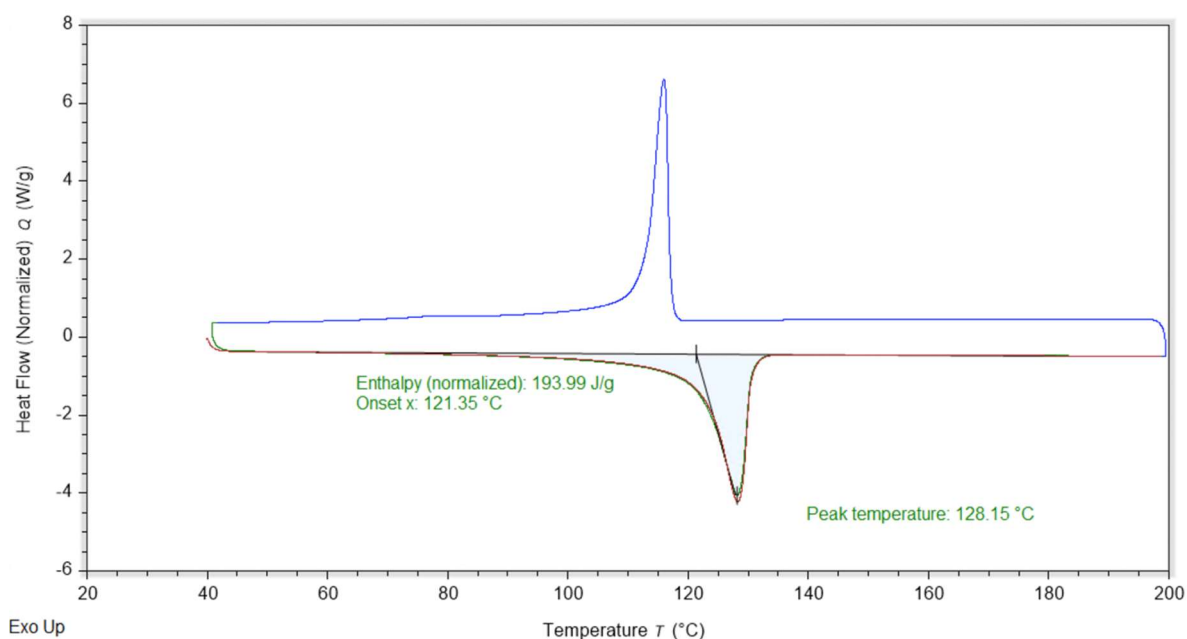


**Figure S96:** Heat flow traces recorded during the third test of **M2**. The initial heating cycle was run at a rate of 10 °C/min, the others performed at a rate of 5 °C/min. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

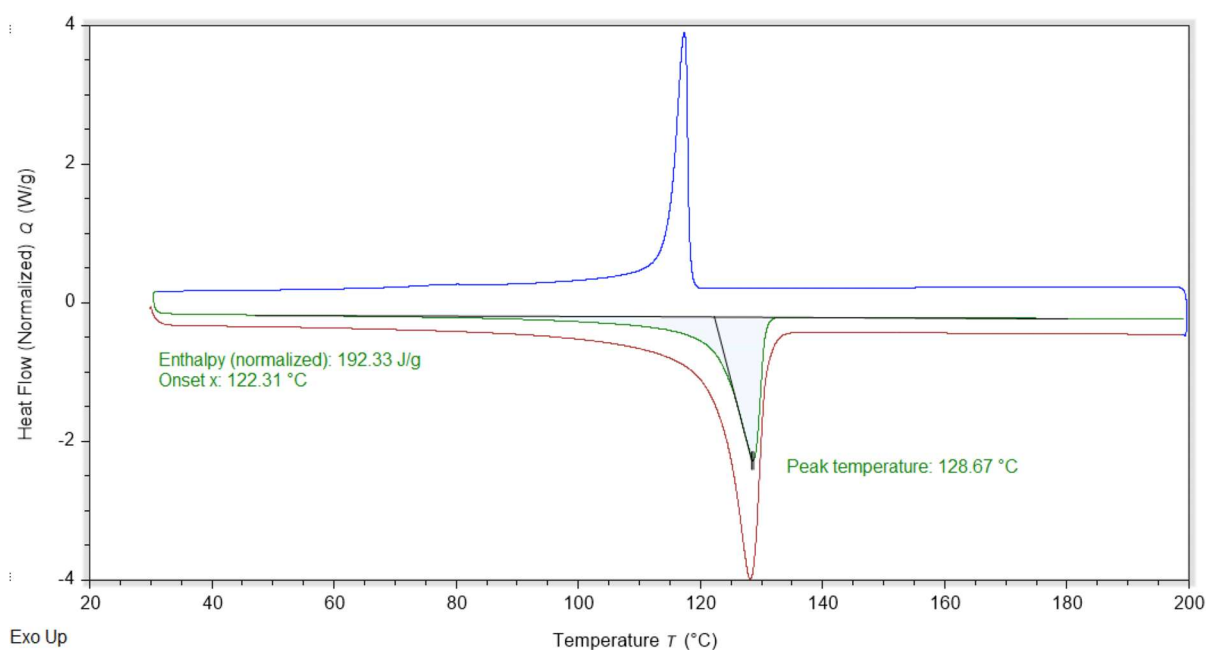
- **M3**



**Figure S97:** Heat flow traces recorded during the first test of **M3** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

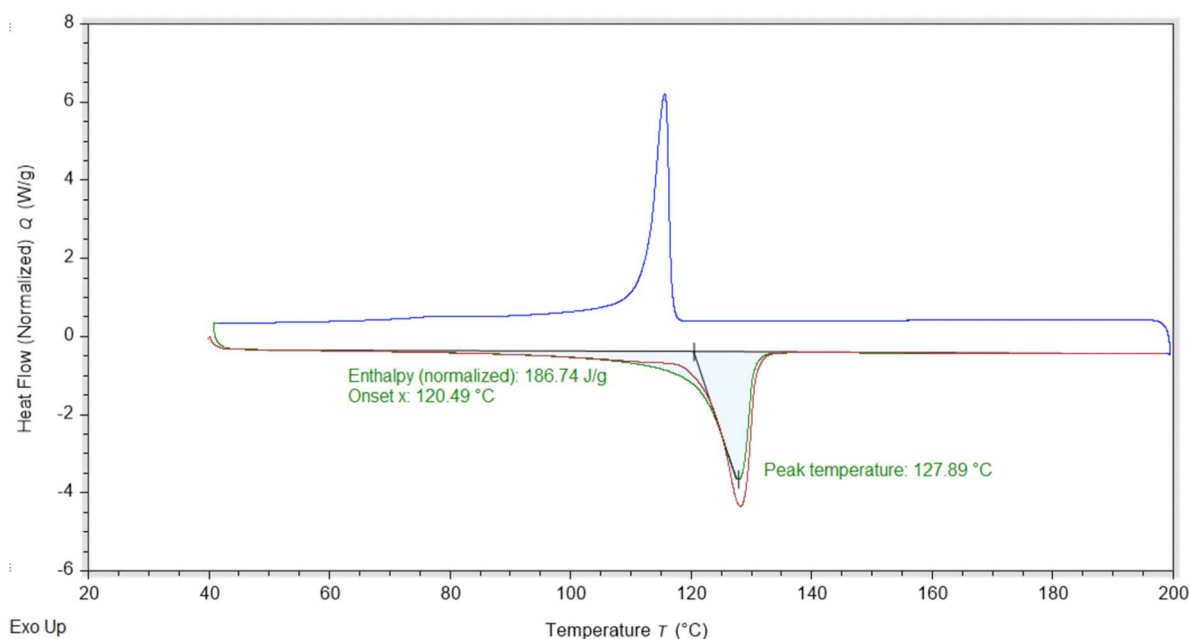


**Figure S98:** Heat flow traces recorded during the second test of **M3** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

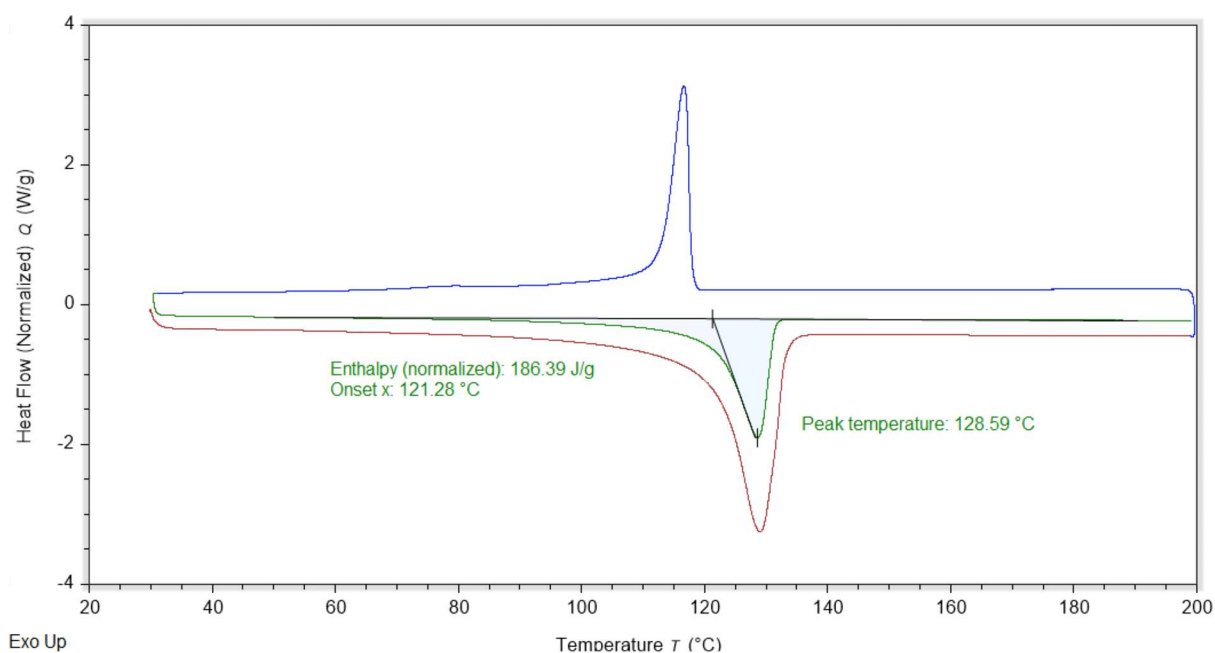


**Figure S99:** Heat flow traces recorded during the third test of **M3**. The initial heating cycle was run at a rate of 10 °C/min, the others performed at a rate of 5 °C/min. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

#### • **M4**

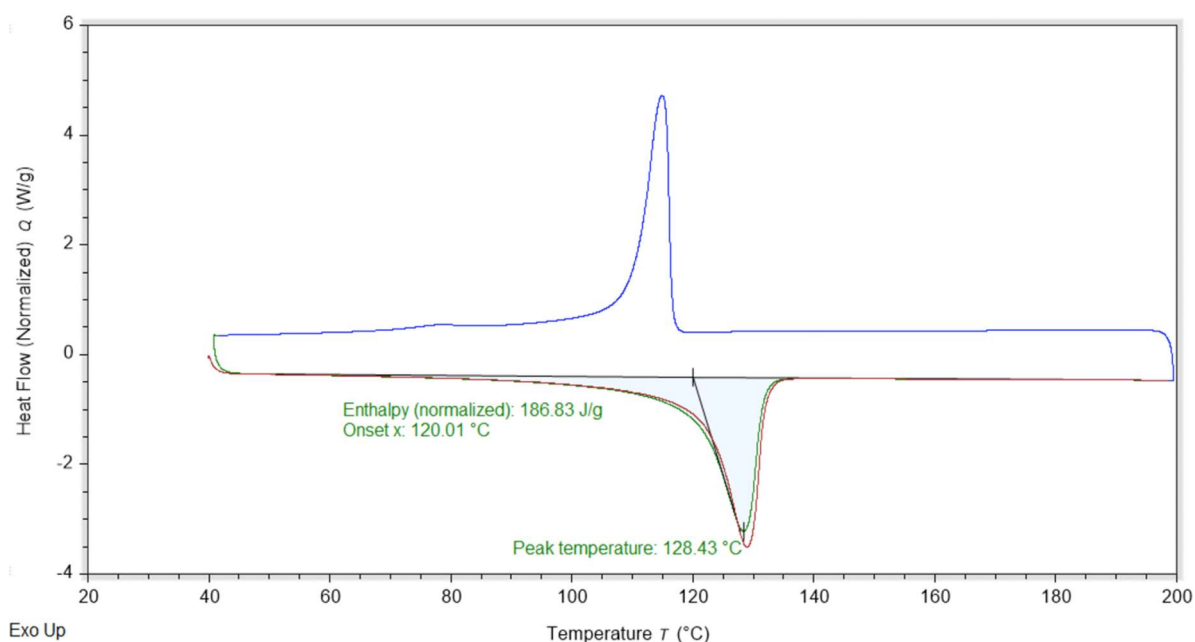


**Figure S100:** Heat flow traces recorded during the first test of **M4** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

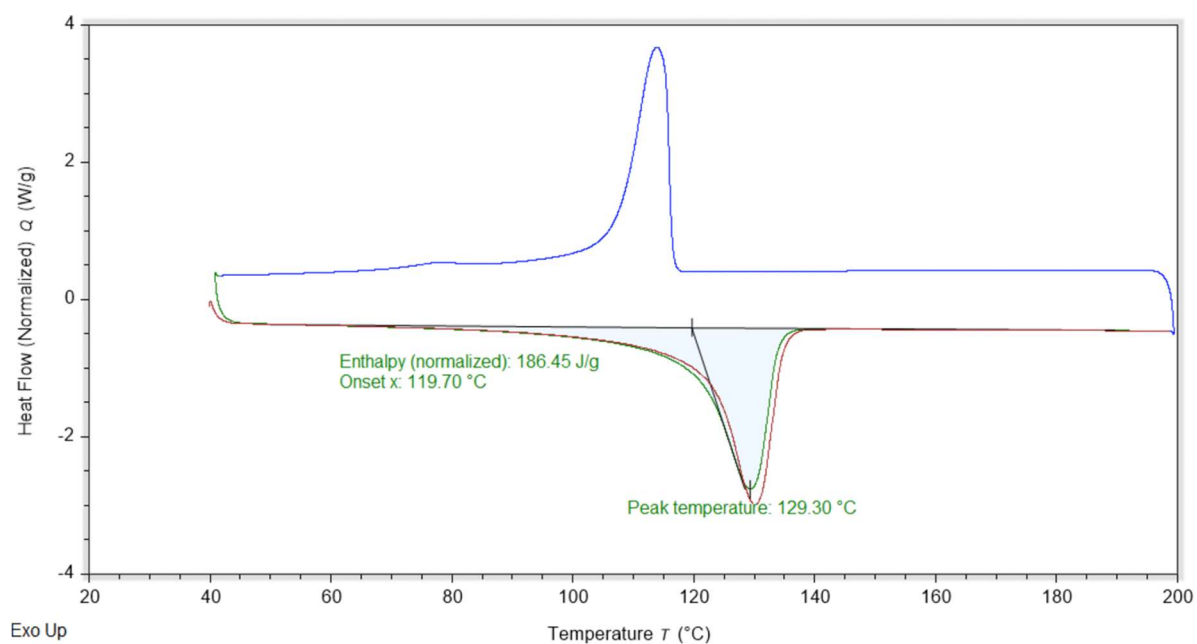


**Figure S101:** Heat flow traces recorded during the second test of **M4**. The initial heating cycle was run at a rate of 10 °C/min, the others performed at a rate of 5 °C/min. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

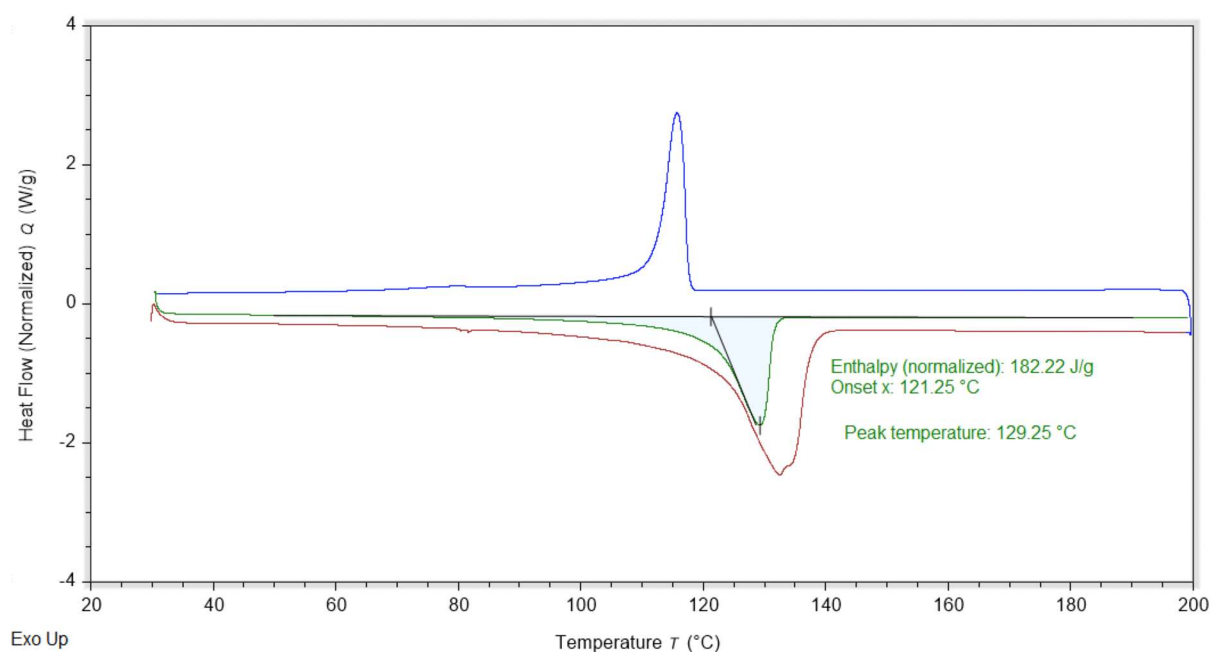
## • **M5**



**Figure S102:** Heat flow traces recorded during the first test of **M5** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

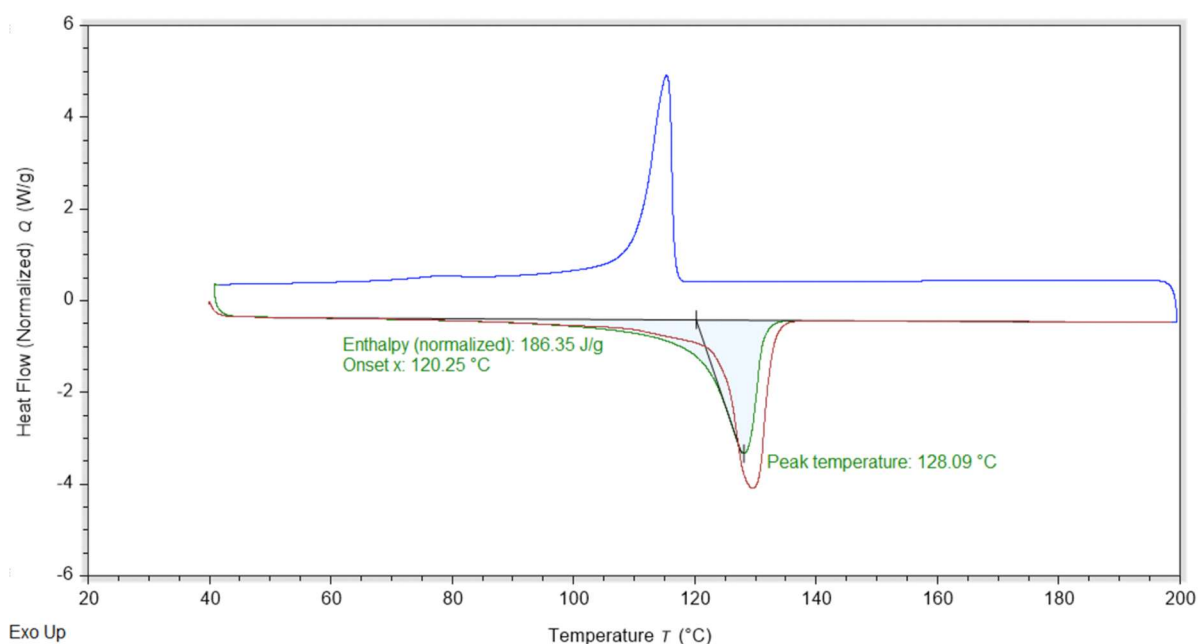


**Figure S103:** Heat flow traces recorded during the second test of **M5** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

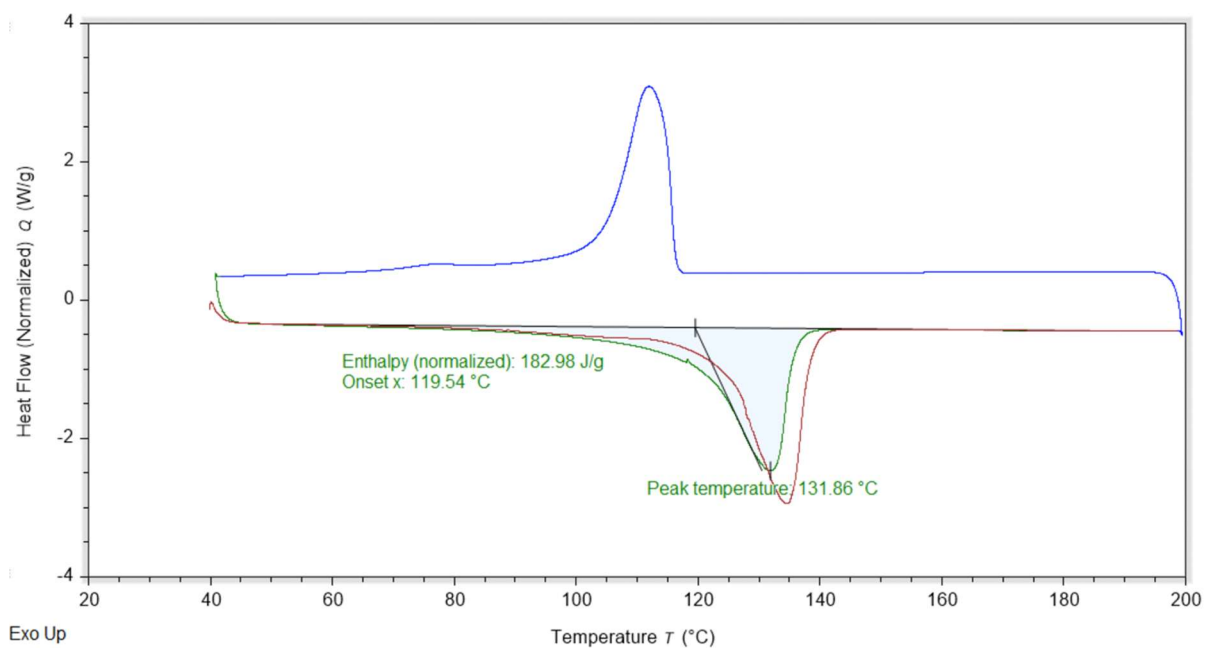


**Figure S104:** Heat flow traces recorded during the third test of **M5**. The initial heating cycle was run at a rate of 10 °C/min, the others performed at a rate of 5 °C/min. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

- **M15**

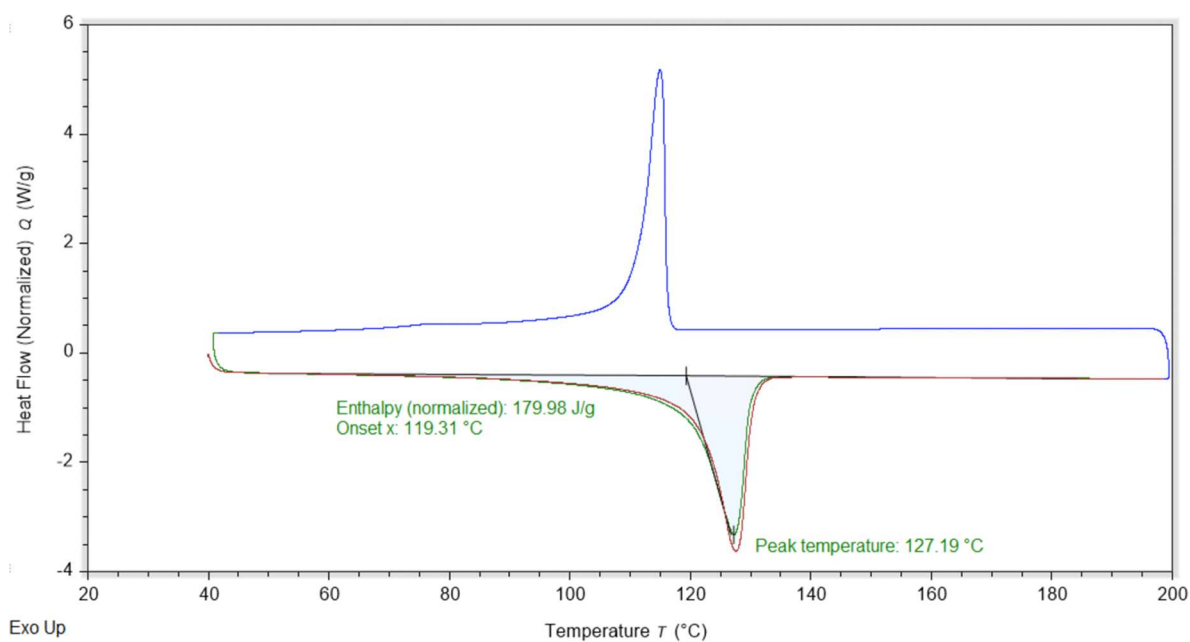


**Figure S105:** Heat flow traces recorded during the first test of **M15** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

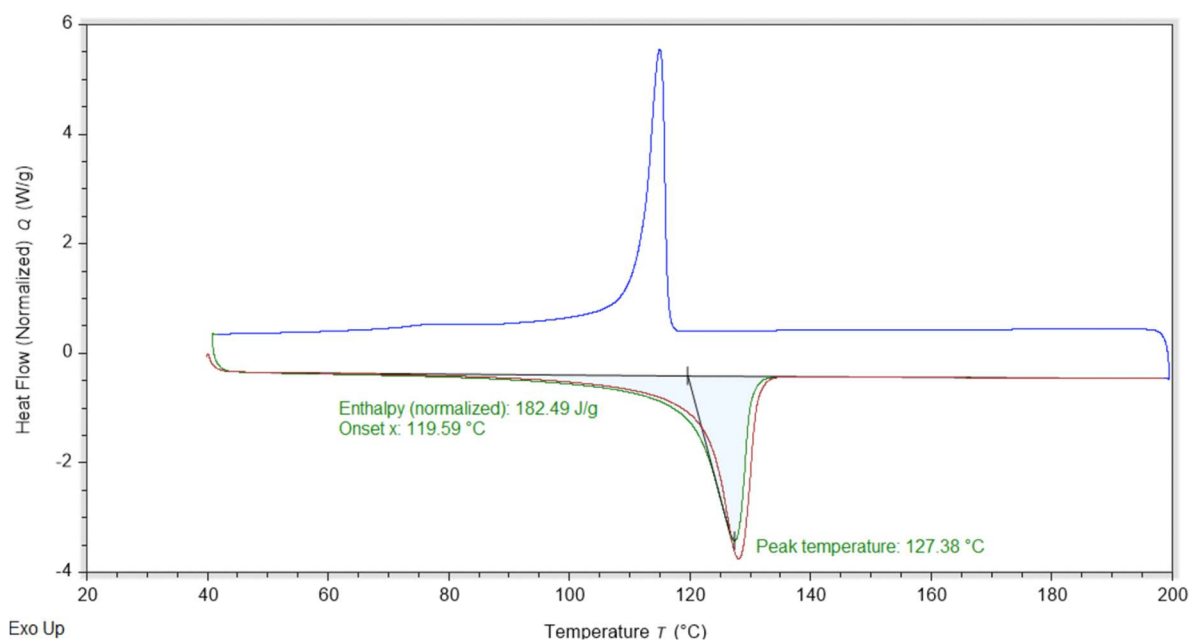


**Figure S106:** Heat flow traces recorded during the second test of **M15** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

- **M16**



**Figure S107:** Heat flow traces recorded during the first test of **M16** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.



**Figure S108:** Heat flow traces recorded during the second test of **M16** as per the stated conditions in Experimental. Red, blue and green traces represent the first heating run, the cooling cycle and the second heating run, respectively.

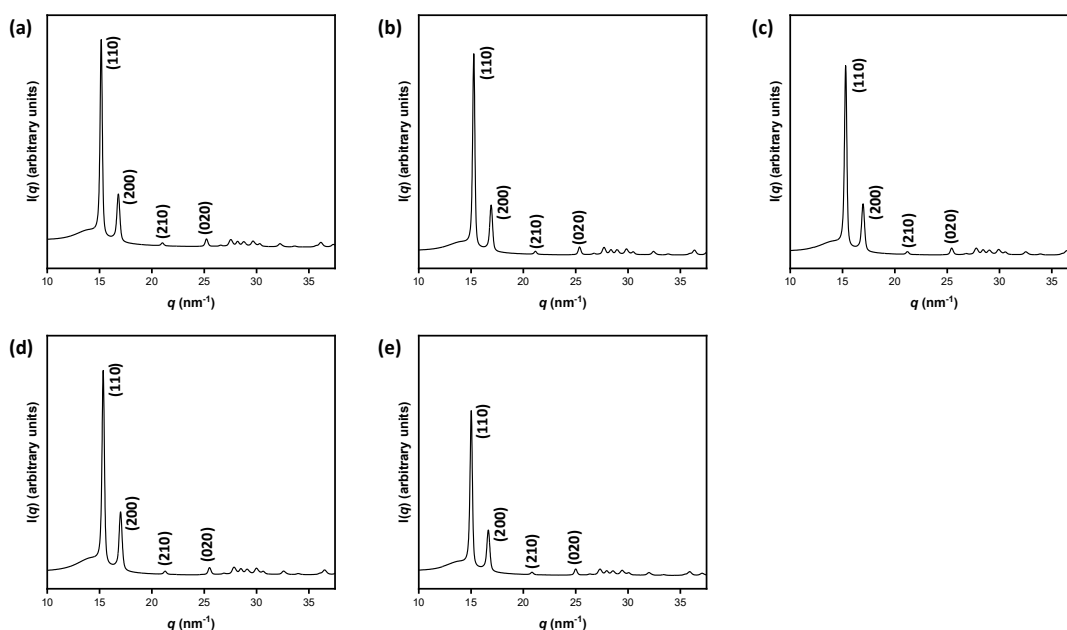


**Table S2:** A summary of the energy change and crystallinity results from the DSC traces. An example calculation is provided in **Calculation S2**.

Sample	Average Melting Enthalpy (J/g)	Standard Deviation ( $\pm$ J/g)	Crystallinity (%)	Propagated Error ( $\pm$ %)
M1	196.5	1.6	67.8	0.6
M2	194.5	1.5	67.0	0.5
M3	191.6	2.9	66.1	1.0
M4	186.6	0.2	64.3	0.1
M5	185.2	2.6	63.9	0.9
M15	184.7	2.4	63.7	0.8
M16	181.2	1.8	62.5	0.6

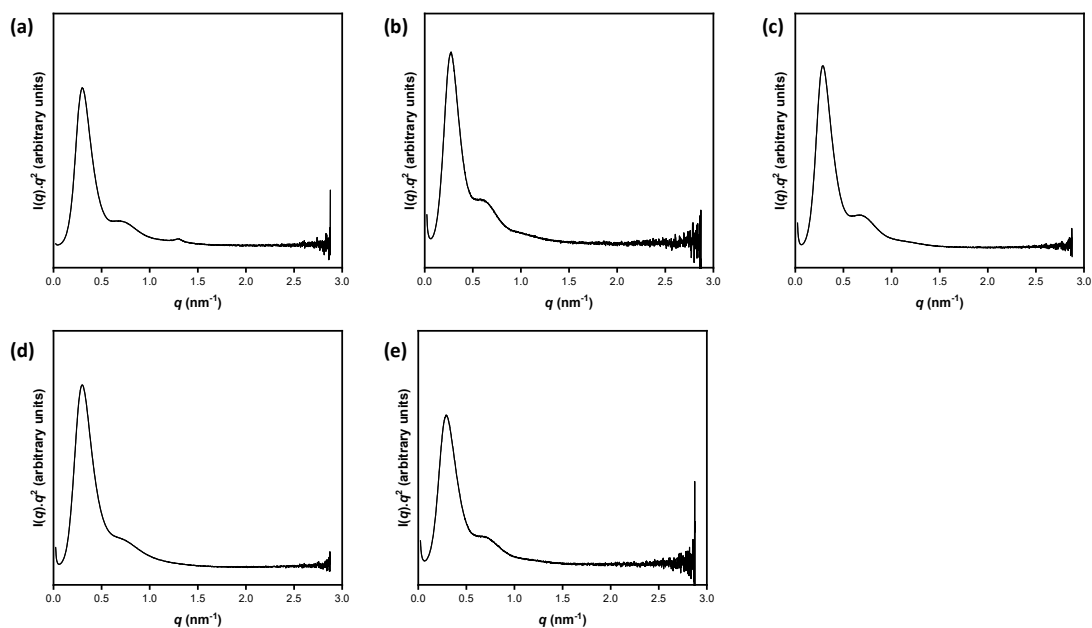
## 6 Wide Angle and Small Angle X-Ray Scattering (WAXS and SAXS) Results

### • WAXS

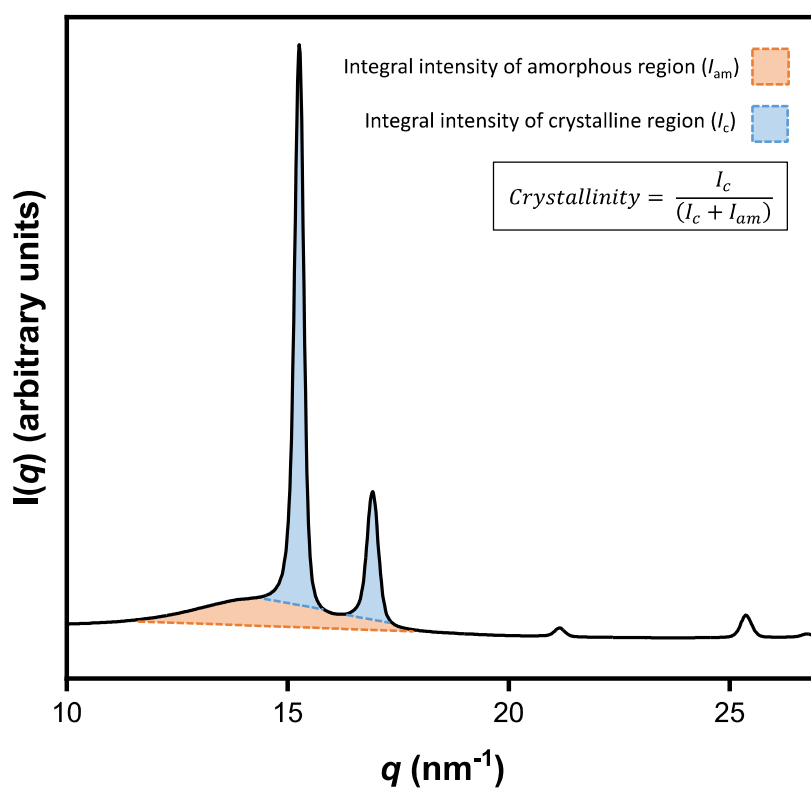


**Figure S109:** WAXS intensity profiles of polymer films (a) M1, (b) M2, (c) M3, (d) M4, and (e) M5, where the peaks in each pattern are annotated with the corresponding reflections of an orthorhombic crystalline structure.

- **SAXS**



**Figure S110:** Lorentz-corrected SAXS intensity profiles of polymer films (a) **M1**, (b) **M2**, (c) **M3**, (d) **M4**, and (e) **M5**.

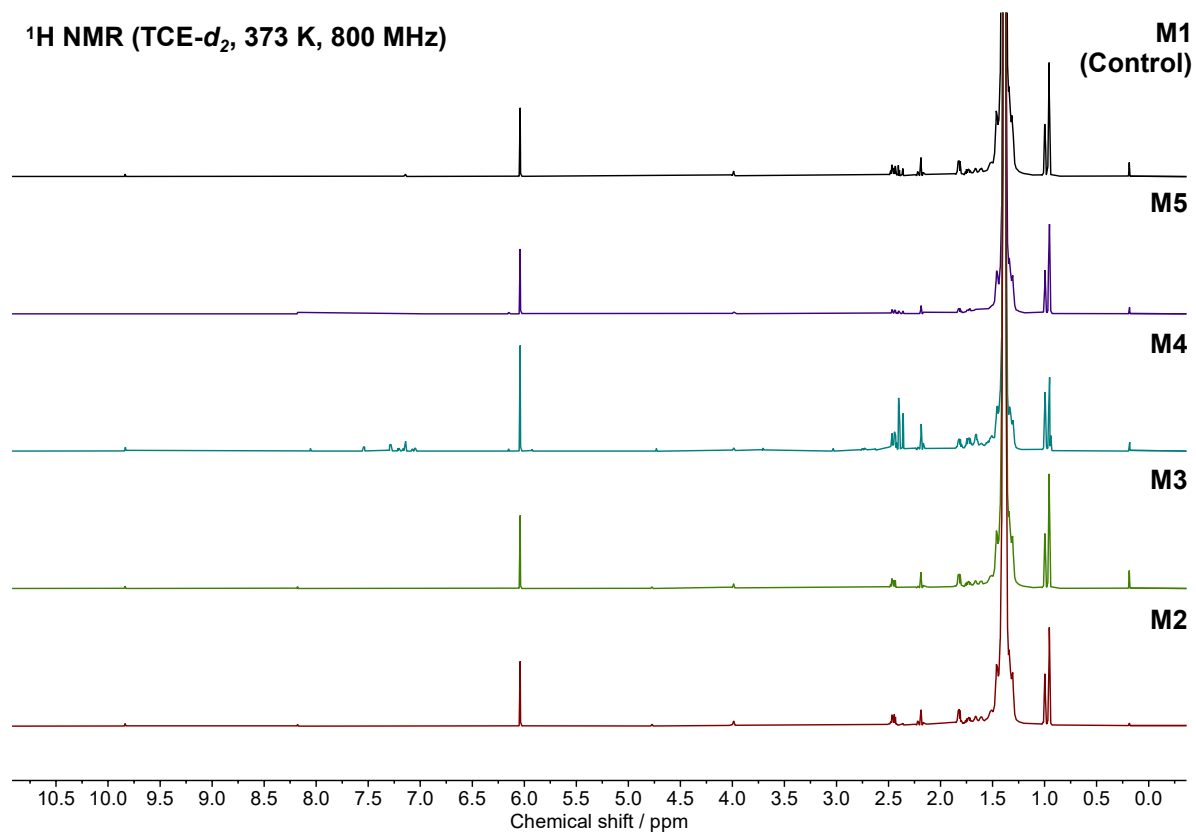


**Figure S111:** Example degree of crystallinity calculation using the WAXS intensity profile for **M2**.

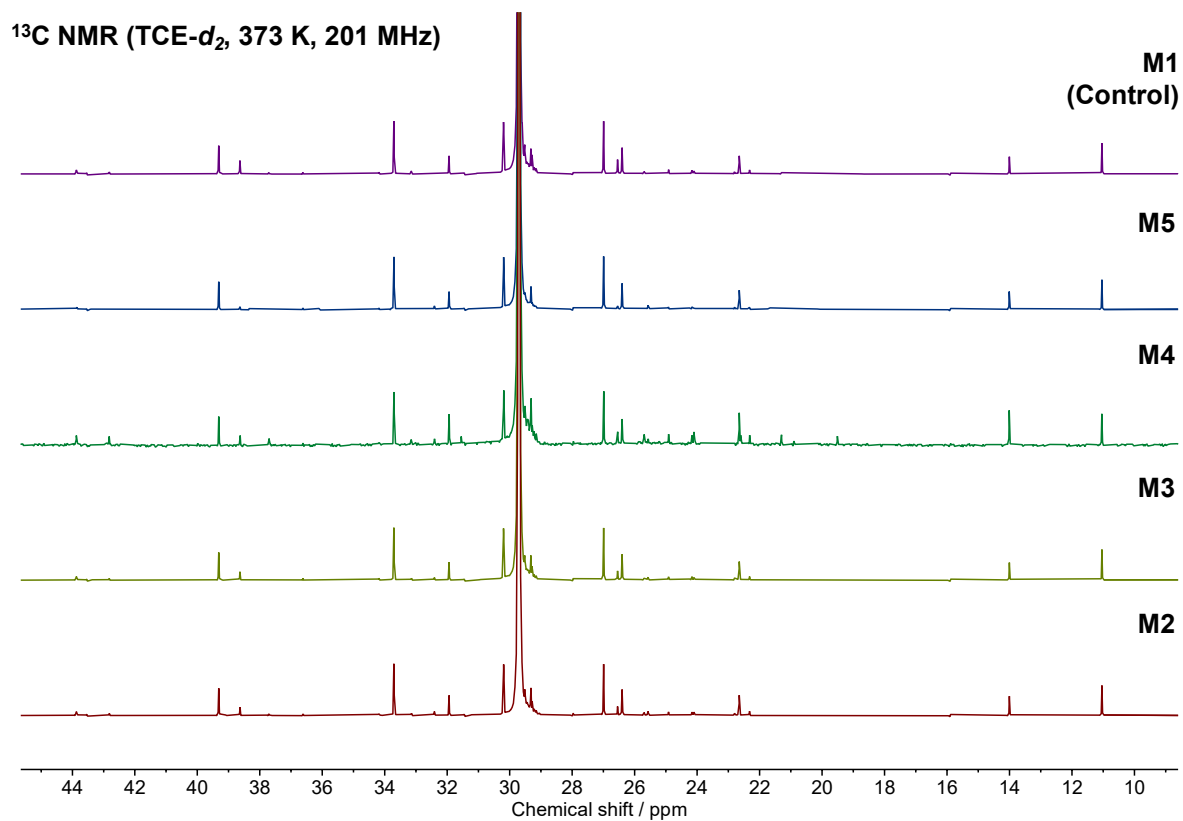
## 7 NMR Spectroscopy Results of the Modified Samples

- M1-M5

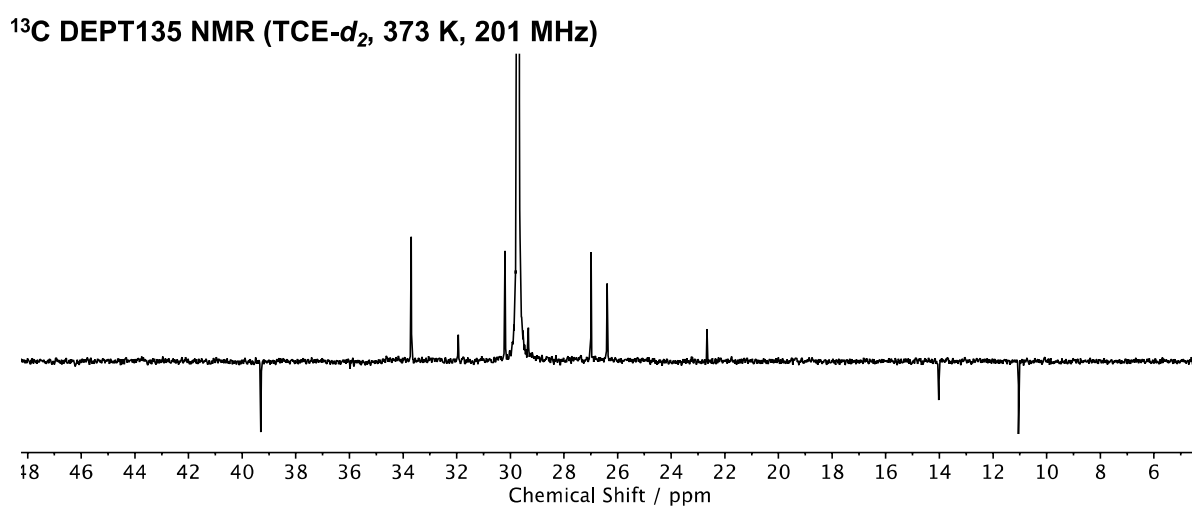
$^1\text{H}$  NMR (TCE- $d_2$ , 373 K, 800 MHz)



**Figure S112:** Stacked  $^1\text{H}$  NMR spectra of **M1-5**.

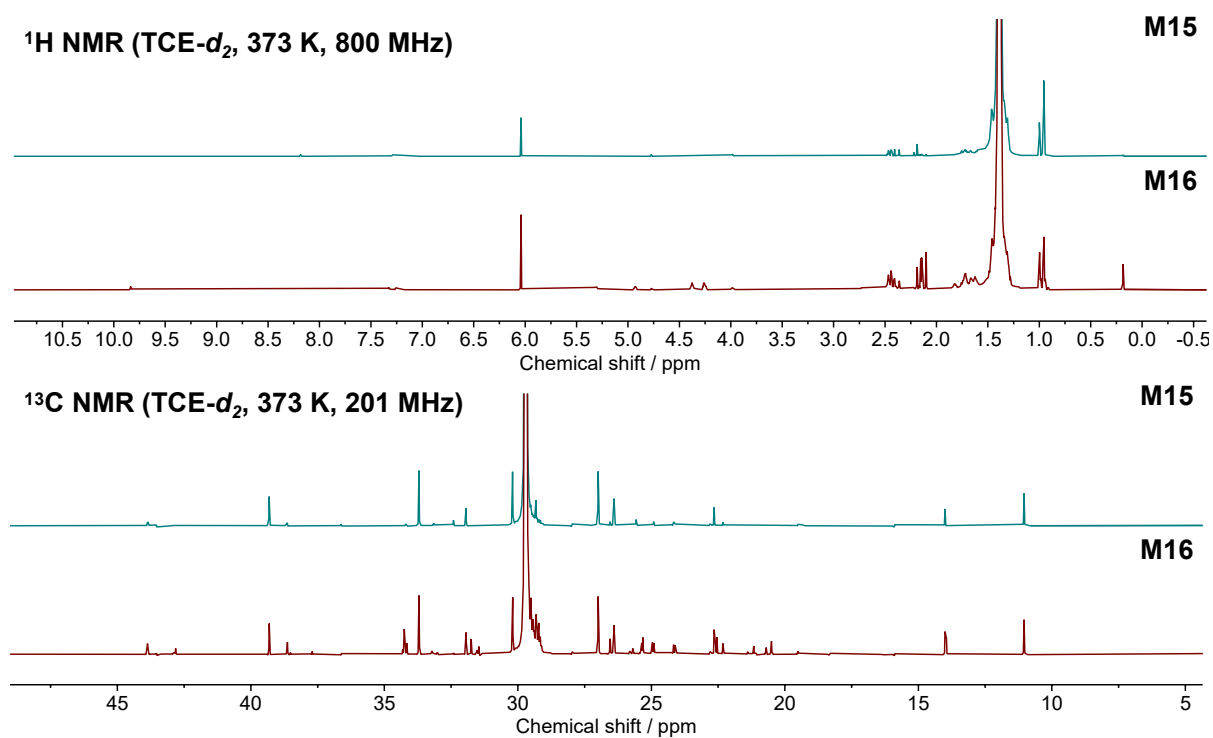


**Figure S113:** Stacked  $^{13}\text{C}$  NMR spectra of **M1-5**.



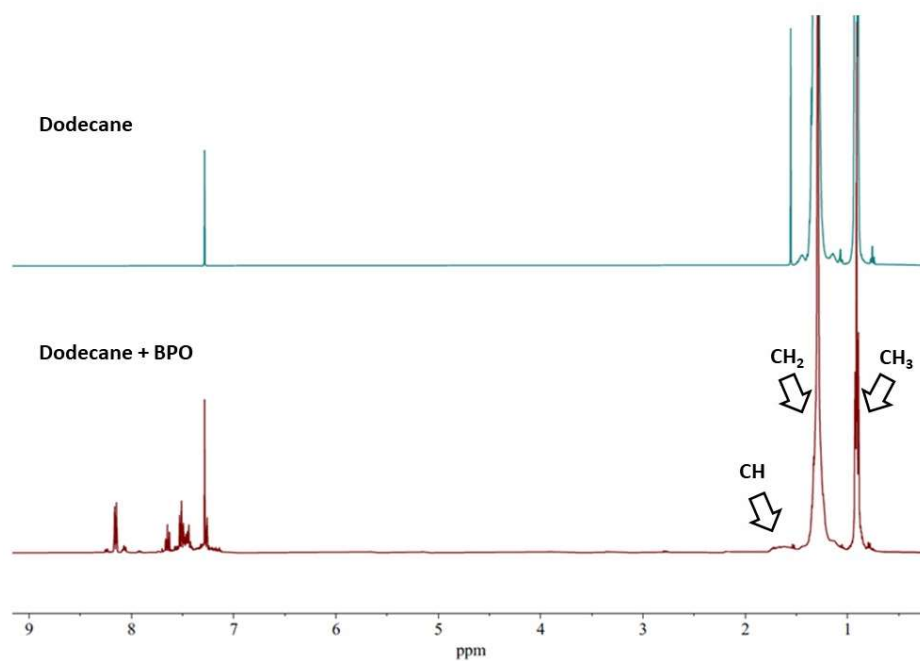
**Figure S114:** The  $^{13}\text{C}$  distortionless enhancement by polarisation transfer (DEPT) NMR spectrum of **M5**.

- **M15 and M16**



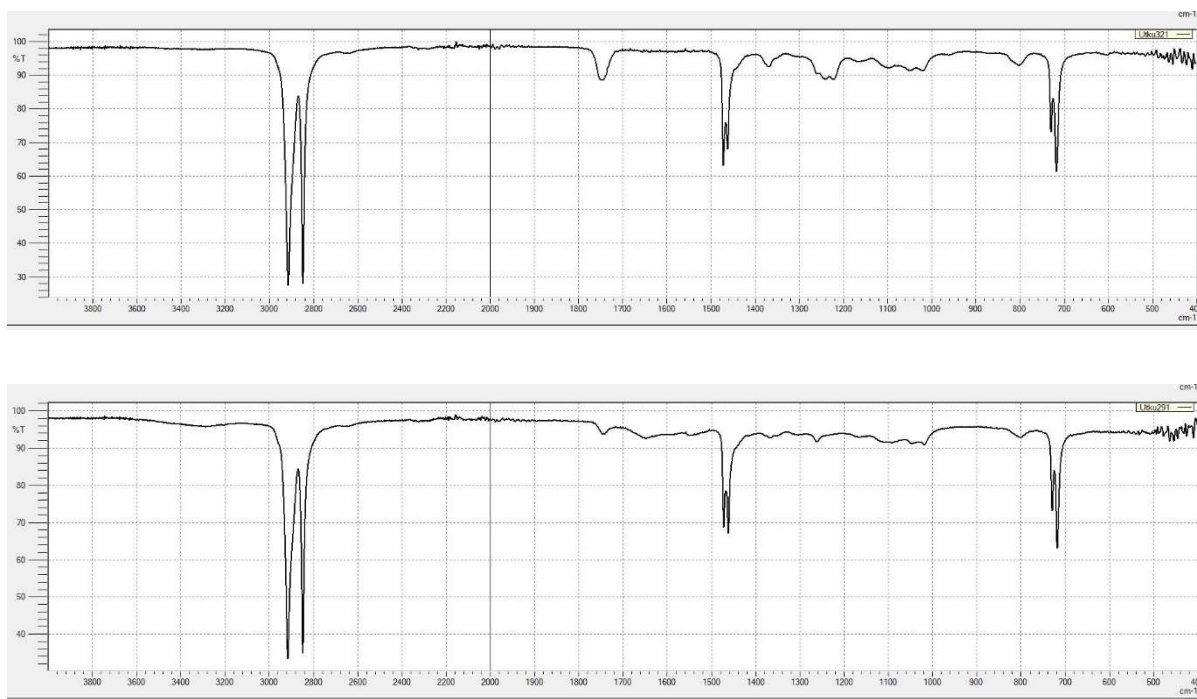
**Figure S115:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **M15** and **M16**.

## 8 Small Molecule Reactivity Studies on *n*-Dodecane



**Figure S116:** Overlaid  $^1\text{H}$  NMR spectrum showing dodecane before (top) and after (bottom) reaction with benzoyl peroxide.

## 9 FT-IR Analysis



**Figure S117:** FT-IR analysis of sample **M1** (control reaction, top) and sample **M5** (6 wt% DLP, bottom), showing the lack of significant oxidation following peroxide modification under N<sub>2</sub> atmosphere. Sample **M5** was selected for comparative purposes as it has the highest peroxide loading of all samples tested.

## 10 References

1. Randall, J. C., A Review of High Resolution Liquid <sup>13</sup>C Carbon Nuclear Magnetic Resonance Characterizations of Ethylene-Based Polymers. *Journal of Macromolecular Science, Part C* **1989**, 29 (2-3), 201-317.