

## Supporting Information

# Chemo-Enzymatic Synthesis of Levoglucosenone-Derived Bi- Functional Monomer and its Ring-Opening Metathesis Polymerization in Green Solvent Cyrene™

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## EXPERIMENTAL SECTION

**Chemical and reagents.** N-LGO<sup>1-3</sup> and N-HBO<sup>4</sup> were synthesized according to literature procedures. Levoglucosenone and Cyrene™ were graciously provided by the Circa group. Novozym® 435 (*Candida antarctica* Lipase B immobilized on a macroporous acrylic resin) was purchased from Novozymes. Vinyl methacrylate was purchased from TCI. Grubbs' 1<sup>st</sup> generation catalyst, Grubbs' 2<sup>nd</sup> generation catalyst and its derivative (C1, C2 and C3 respectively), Hoveyda-Grubbs catalyst (C4), ethyl vinyl ether, were purchased from Sigma Aldrich. The NMR solvent CDCl<sub>3</sub> was purchased from Cambridge Isotopes Laboratories. All chemicals and reagents were used as received without purification unless mentioned.

**Characterization.** *Nuclear Magnetic Resonance (NMR) spectroscopy.* <sup>1</sup>H NMR spectra were recorded on a Bruker Fourier 300 MHz (CDCl<sub>3</sub> residual signal at 7.26). <sup>13</sup>C NMR spectra were recorded at 75 MHz (CDCl<sub>3</sub> residual signal at 77.16 ppm). Chemical shifts are given in parts per million (ppm).

*Gas chromatography-mass spectrometry (GC-MS)* of N-HBO-MA was performed using an AgilentGC 5975 coupled with MS 7890 in an electron impact mode with electron energy set at 70 eV and a mass range atm/z (30–350 amu). A HP5-MS capillary column (Agilent, 30 m × 0.25 mm, 0.25 μm) was used for chromatographic separation. The injection was performed at 280 °C in split mode (10:1), being injected 1 μL of the sample. The oven temperature program was the following: from 35 °C held for 2 min, then raised until 300 °C at 20 °C/min with a 5 min hold. The hydrogen flow rate was set at 1.2 mL/min. The mass detector was set as follows: source and quad temperatures at 230 and 150 °C, respectively.

*Size exclusion chromatography (SEC)* was performed at 50 °C using an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector, a viscometer detector, a laser, UV lamp and two PLgel columns (5 μm MIXED-D 300

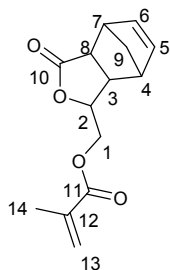
x 7.5 mm) using 10 mM Lithium Bromide in HPLC grade dimethylformamide as the mobile phase at a flow rate of 1.0 mL/min. Calibration was performed with poly(methyl methacrylate) Standards.

*Thermogravimetric Analysis (TGA)* was measured with a TGA Q500 (TA Instruments). Typically, ~1 mg of each sample was equilibrated at 50 °C for 30 min and was flushed with highly pure nitrogen gas. All the experiments were performed with a heating rate of 10 °C/min up to 600 °C. The reported values  $T_{d5\%}$  and  $T_{d50\%}$  represent the temperature at which 5% and 50% of the mass is lost, respectively.

*Differential Scanning Calorimetry (DSC)* thermograms were obtained with a DSC Q20 (TA Instruments). Typically, ~5 mg sample was placed in a sealed pan, flushed with highly pure nitrogen gas and passed through a heat-cool-heat cycle at 10 °C/min in a temperature range of -80 °C to 250 °C.

*Dynamic mechanical analysis (DMA)* of polymer films was performed with a DMA Q800 (TA Instrument) in tension deformation mode. The frequency was set to 1 Hz and strain to 0.06 %. The temperature was raised from -140 °C to 180 °C at 3 °C/min.

**Synthesis of N-HBO-MA.** A mixture of N-HBO (3.6 g, 20 mmol), vinyl methacrylate (7.2 mL, 60 mmol) and Novozym<sup>®</sup> 435 (15 wt%) was stirred at 50 °C for 2 h. The reaction mixture was suspended in acetone (50 mL) and filtered through a plug of celite. The filtrate was concentrated to dryness and the residue was purified by silica gel chromatography (gradient: 90/10 to 50/50 cyclohexane/ethylacetate as eluant) to give 4.4 g of N-HBO-MA (90%, white solid).



Melting point: 82-83 °C

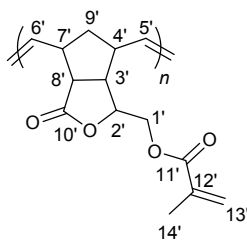
$[\alpha]_D$  (0.05 M, Chloroform) =  $-42.3^\circ$

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 6.31 (dd,  $J = 2.7$  and  $5.7$  Hz, 1H,  $\text{H}_6$ ), 6.27 (dd,  $J = 2.7$  and  $5.7$  Hz, 1H,  $\text{H}_5$ ), 6.10 (s, 1H,  $\text{H}_{13}$ ), 5.60 (t,  $J = 1.5$  Hz, 1H,  $\text{H}_{13}$ ), 4.25 (dd,  $J = 1.5$  and  $3.6$  Hz, 2H,  $\text{H}_1$ ), 4.19 (t,  $J = 1.7$  Hz, 1H,  $\text{H}_2$ ), 3.33 (broad s, 1H,  $\text{H}_7$ ), 3.28 (dd,  $J = 4.2$  and  $8.7$  Hz, 1H,  $\text{H}_8$ ), 3.14 (broad s, 1H,  $\text{H}_4$ ), 2.88 (dt,  $J = 1.9$  and  $9.1$  Hz, 1H,  $\text{H}_3$ ), 1.94 (s, 3H,  $\text{H}_{14}$ ), 1.64 (dt,  $J = 1.5$  and  $8.7$  Hz, 1H,  $\text{H}_{9s}$ ), 1.44 (d,  $J = 8.7$  Hz, 1H,  $\text{H}_{9a}$ ).

$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 177.4 (C=O,  $\text{C}_{10}$ ), 167.2 (C=O,  $\text{C}_{11}$ ), 137.1 (CH=C,  $\text{C}_6$ ), 135.7 (C=CH<sub>2</sub>,  $\text{C}_{12}$ ), 134.5 (CH=C,  $\text{C}_5$ ), 126.7 (CH<sub>2</sub>=C,  $\text{C}_{13}$ ), 79.4 (CH-O,  $\text{C}_2$ ), 66.2 (CH<sub>2</sub>-O,  $\text{C}_1$ ), 51.8 (CH<sub>2</sub>,  $\text{C}_9$ ), 48.4 (CH,  $\text{C}_7$ ), 46.0 (CH,  $\text{C}_8$ ), 45.8 (CH,  $\text{C}_4$ ), 43.2 (CH,  $\text{C}_3$ ), 18.4 (CH<sub>3</sub>,  $\text{C}_{14}$ ).

**Metathesis polymerization of N-HBO-MA** (*typical procedure, entry 3, Table 1*). A Schlenk flask was charged with N-LGO (100 mg, 0.43 mmol) followed by three purges of vacuum/nitrogen. Cyrene™ (0.31 mL, the minimal quantity required to ensure the complete dissolution of the monomer) was added and the mixture was stirred at ambient temperature for 10 min. A stock solution of C4 in Cyrene™ (0.02 M) was prepared by dissolving 20.1 mg of the C4 in Cyrene™ (1.6 mL) at 60 °C (at ambient temperature the catalyst is not soluble). Upon dissolution of N-HBO-MA, 120  $\mu\text{L}$  of the stock solution was added to the reaction flask and stirred for 8 min. At the end of the reaction, the medium was viscous, the polymerization was quenched by adding ethyl vinyl ether (4  $\mu\text{L}$ , 20 eq with respect to C4) in DCM (0.5 mL). An aliquot of the obtained solution was taken and evaporated to dryness to determine the extent

of conversion by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ . The solution was precipitated from methanol (25 mL). The formed solid polymer was vacuum dried at ambient temperature for 72 h.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 6.09 (1H,  $\text{H}_{13'}$ ), 5.70 (1H,  $\text{H}_{6'}$ ), 5.59 (1H,  $\text{H}_{13'}$ ), 5.53 (1H,  $\text{H}_{5'}$ ), 4.75 (1H,  $\text{H}_{2'}$ ), 4.36 (2H,  $\text{H}_{1'}$ ), 3.09-2.83 (4H,  $\text{H}_{7'}$ ,  $\text{H}_{8'}$ ,  $\text{H}_{3'}$  and  $\text{H}_{4'}$ ), 1.98 (1H,  $\text{H}_{9's}$ ), 1.92 (3H,  $\text{H}_{13'}$ ), 1.47 (1H,  $\text{H}_{9'a}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 175.6 ( $\text{C}=\text{O}$ ,  $\text{C}_{10'}$ ), 167.0 ( $\text{C}=\text{O}$ ,  $\text{C}_{11'}$ ), 135.7 ( $\text{C}=\text{CH}_2$ ,  $\text{C}_{12'}$ ), 131.9-129.4 ( $\text{CH}=\text{CH}$ ,  $\text{C}_{6'}$  and  $\text{C}_{5'}$ ), 126.7 ( $\text{CH}_2=\text{C}$ ,  $\text{C}_{13'}$ ), 77.4 ( $\text{CH}-\text{O}$ ,  $\text{C}_{2'}$ ), 66.2 ( $\text{CH}_2-\text{O}$ ,  $\text{C}_{1'}$ ), 49.0 ( $\text{CH}_2$ ,  $\text{C}_{9'}$ ), 48.7 ( $\text{CH}$ ,  $\text{C}_{7'}$ ), 46.1 ( $\text{CH}$ ,  $\text{C}_{8'}$ ), 45.4 ( $\text{CH}$ ,  $\text{C}_{4'}$ ), 40.8 ( $\text{CH}$ ,  $\text{C}_{3'}$ ), 18.8 ( $\text{CH}_3$ ,  $\text{C}_{14'}$ ).

**Preparation of films.** Polymer films were obtained by solvent casting. A 1 %w/w solution of P(N-HBO-MA) in chloroform was poured into a 1.5 mm x 8 mm x 40 mm mold. Control over the film thickness, measured by electronic digital caliper, was achieved by successive addition of the prepared polymer solution into the mold after solvent removal. Slow evaporation of the solvent allowed the access to more uniform films with no (or less) voids.

**Table S1.** Calculation of  $E$  factor<sup>5</sup> of the polymerization entries reported in Table 1

Entry	Input		Equivalent Ratios	M (g/mol)	Input Volume (ml)	Density (g/cm <sup>3</sup> )	m (mg)	n (mmol)	Output	Output Weight (mg)	% yield	ROMP $E$ factor <sup>a</sup>	Cyrene contribution % <sup>b</sup>	process $E$ Factor <sup>c</sup>
1	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100	5.4	84	210.1
		C2	1	848.97	-	-	1.8	0.002						
		Cyrene™	1951	128.13	0.43	1.25	537.5	4.19						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
	Purification	Methanol	287431	32.04	25	0.79	19800	618						
2	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	65	65	8.8	84	323.7
		C3	1	792.87	-	-	1.7	0.0022						
		Cyrene™	1951	128.13	0.43	1.25	537.5	4.19						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
	Purification	Methanol	287431	32.04	25	0.79	19800	618						
3	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100	5.4	84	210.1
		C4	1	626.62	-	-	1.3	0.002						
		Cyrene™	1951	128.13	0.43	1.25	537.5	4.19						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
	Purification	Methanol	287431	32.04	25	0.79	19800	618						
4	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100	7.6	88	212.3
		C2	1	848.97	-	-	1.8	0.002						
		Cyrene™	2767	128.13	0.61	1.25	762.5	5.95						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						

	Purification	Methanol	287431	32.04	25	0.792	19800	618						
5	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	67	67	11.9	88	317.4
		C3	1	792.87	-	-	1.7	0.002						
		Cyrene™	2767	128.13	0.61	1.25	762.5	5.95						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
Purification	Methanol	287431	32.04	25	0.79	19800	618							
6	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100	7.6	88	212.3
		C4	1	626.62	-	-	1.3	0.002						
		Cyrene™	2767	128.13	0.61	1.25	762.5	5.95						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
Purification	Methanol	287431	32.04	25	0.79	19800	618							
7	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100	13.5	93	218.2
		C2	1	848.97	-	-	1.8	0.002						
		Cyrene™	4900	128.13	1.08	1.25	1350	10.53						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
Purification	Methanol	287431	32.04	25	0.79	19800	618							
8	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	68	68	20.3	93	321.4
		C3	1	792.87	-	-	1.7	0.002						
		Cyrene™	4900	128.13	1.08	1.25	1350	10.53						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
Purification	Methanol	287431	32.04	25	0.79	19800	618							
9	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100	13.5	93	218.2
		C4	1	626.62	-	-	1.3	0.002						
		Cyrene™	4900	128.13	1.08	1.25	1350	10.53						

	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.04						
		DCM	3641	84.93	0.5	1.33	665	7.83						
	Purification	Methanol	287431	32.04	25	0.79	19800	618						
10	ROMP	N-HBO-MA	200	234.25	-	-	100	0.43	P(N-HBO-MA)	100	100 <sup>f</sup>	107.5	99	312.2
		C4	1	626.62	-	-	1.3	0.002						
		Cyrene™	39022	128.13	8.6	1.25	10750	83.89						
	Termination	EVE <sup>e</sup>	20	72.11	0.004	0.75	3.1	0.043						
		DCM	3641	84.93	0.5	1.33	665	7.830						
	Purification	Methanol	287431	32.04	25	0.79	19800	618						

$${}^a \text{ROMP } E \text{ factor} = \frac{m(N-HBO-MA) + m(\text{catalyst}) + m(\text{cyrene}) - m(\text{polymer})}{m(\text{polymer})}$$
. <sup>b</sup> Cyrene™ contribution to the ROMP *E* factor. <sup>c</sup> The process *E* factor including the termination and purification reagents. <sup>e</sup> Ethyl vinyl ether (EVE) used as a termination reagent. <sup>f</sup> Assuming 100% monomer conversion.



➤ NMR data

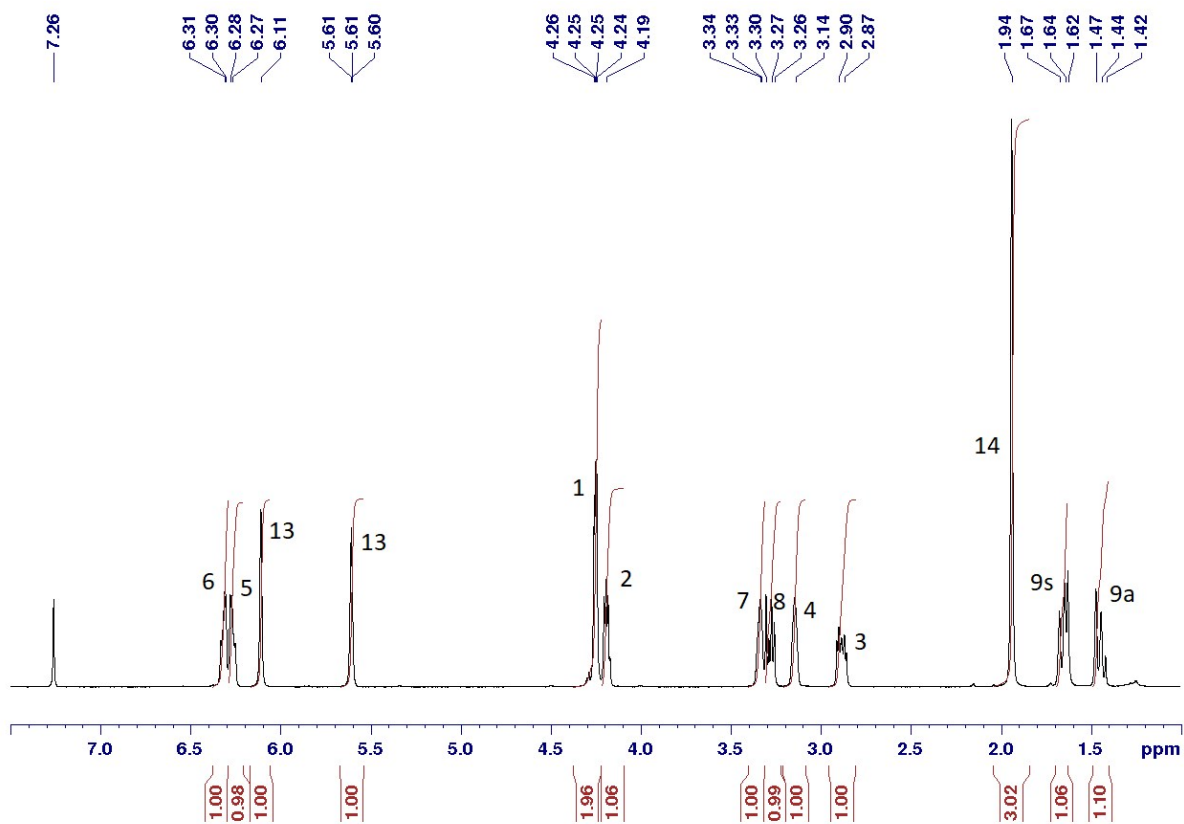


Figure S1. <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of N-HBO-MA

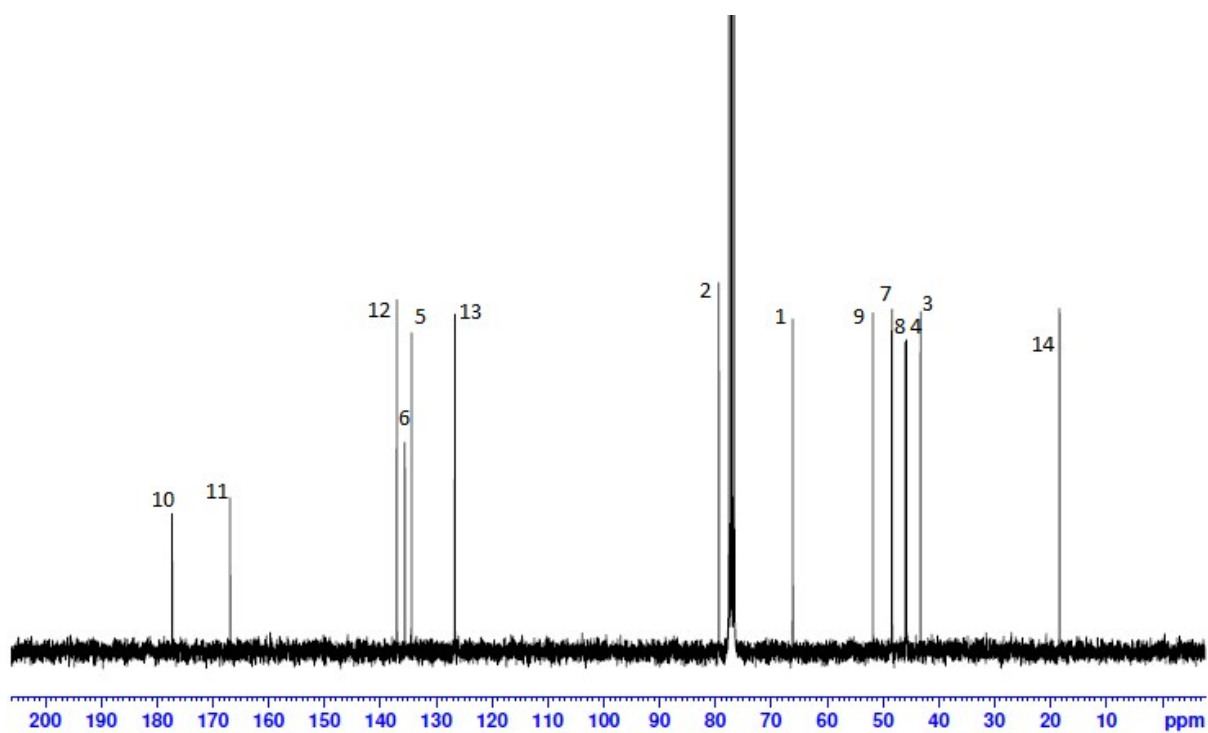


Figure S2.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) spectrum of N-HBO-MA

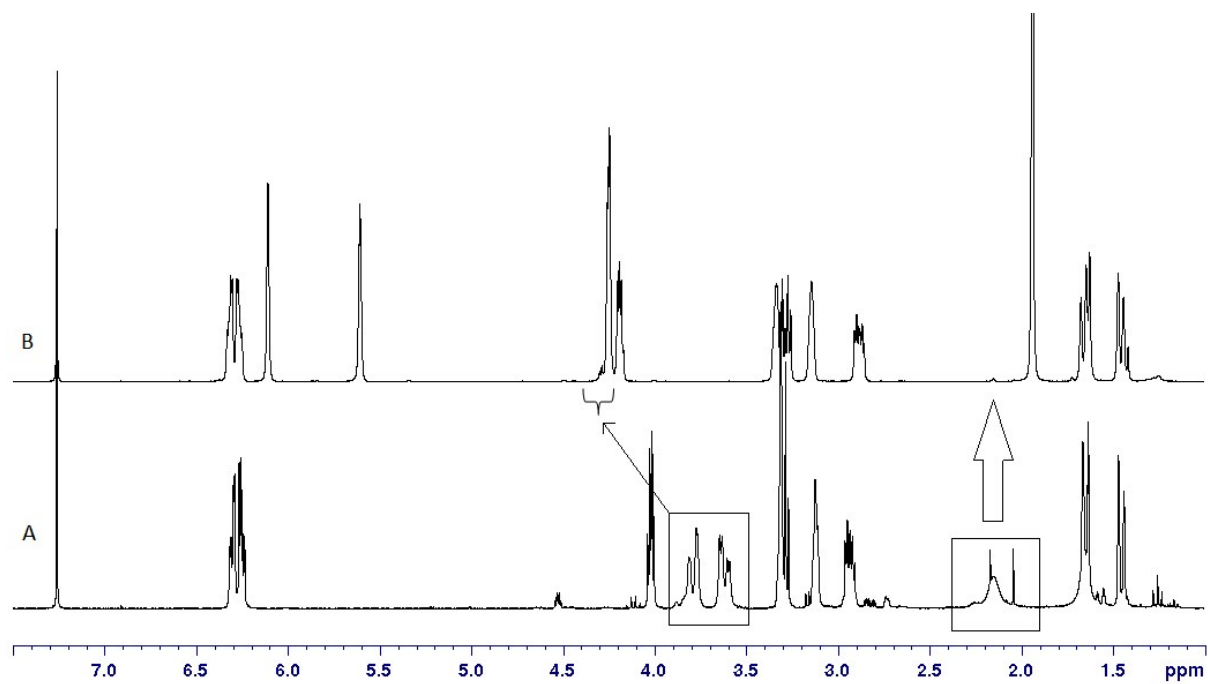


Figure S3.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectra of N-HBO (A) and N-HBO-MA (B)

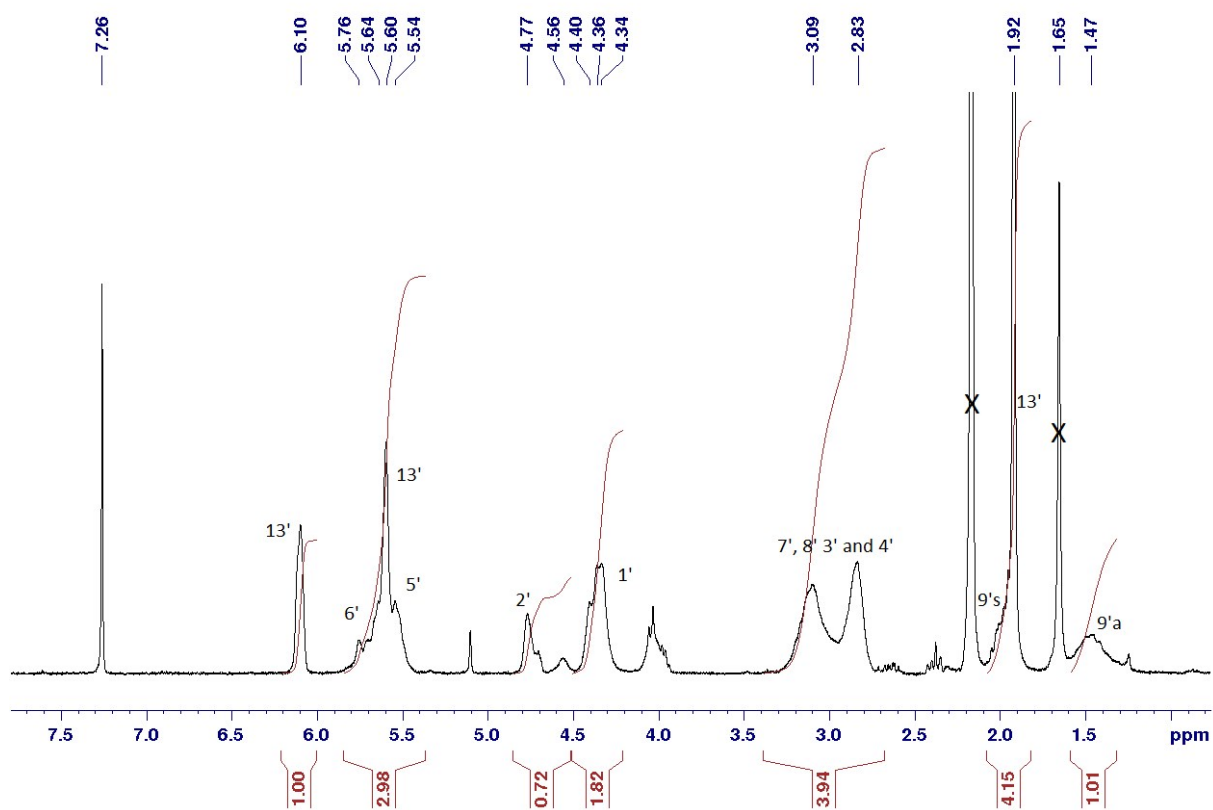


Figure S4.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of P(N-HBO-MA) (entry 3, Table 1)

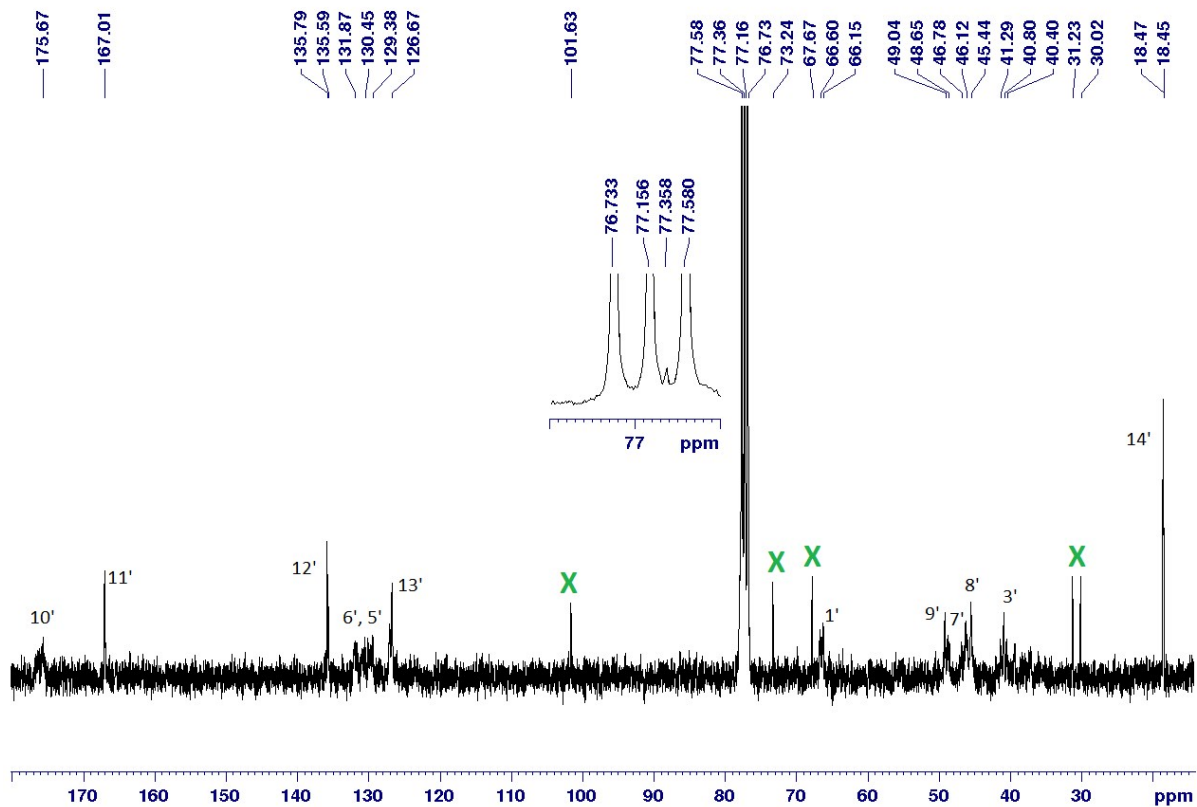
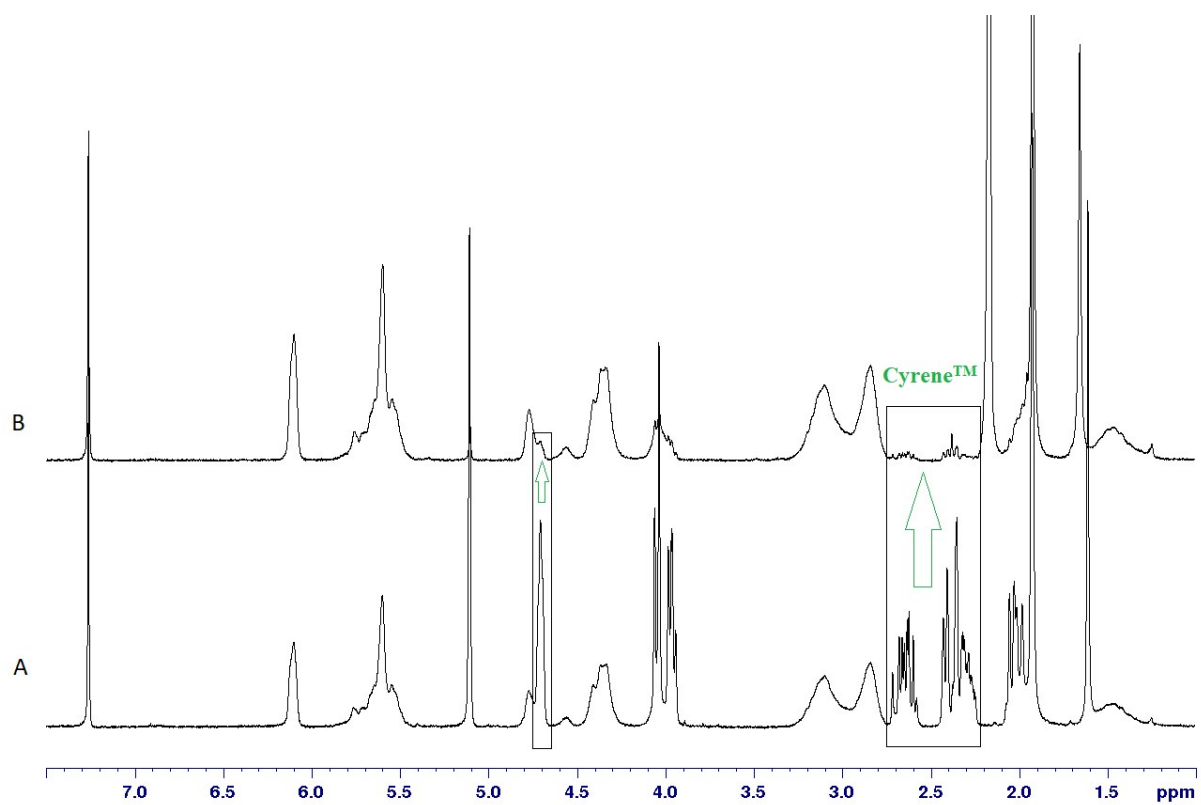
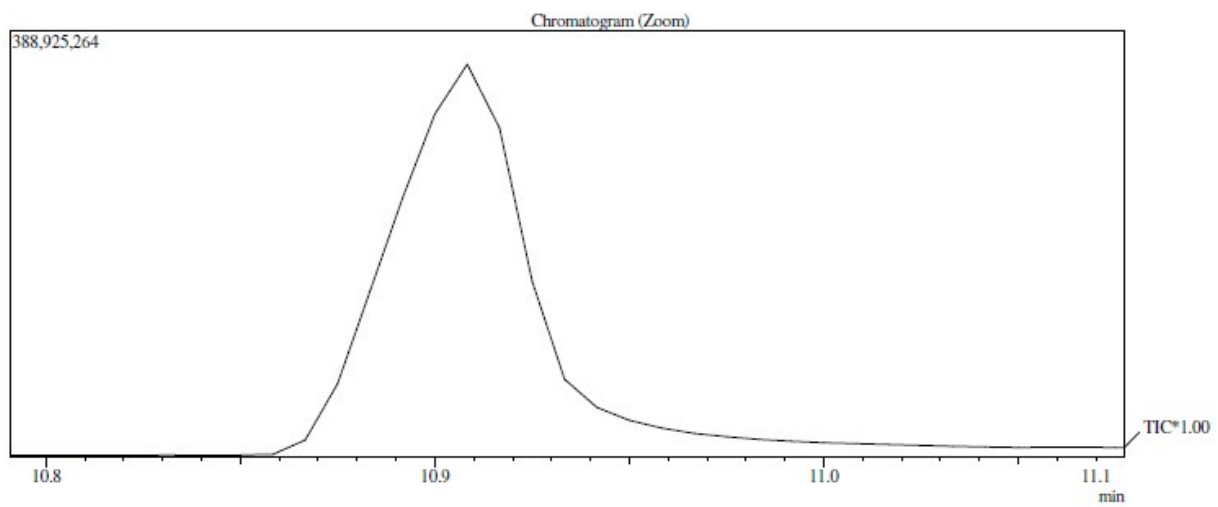
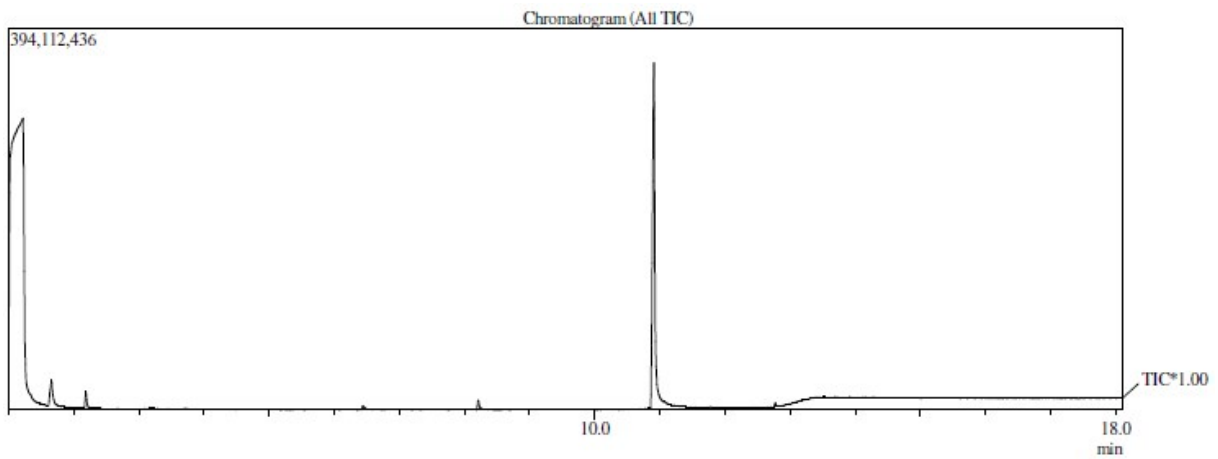


Figure S5.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) spectrum of P(N-HBO-MA) (entry 3, Table 1)



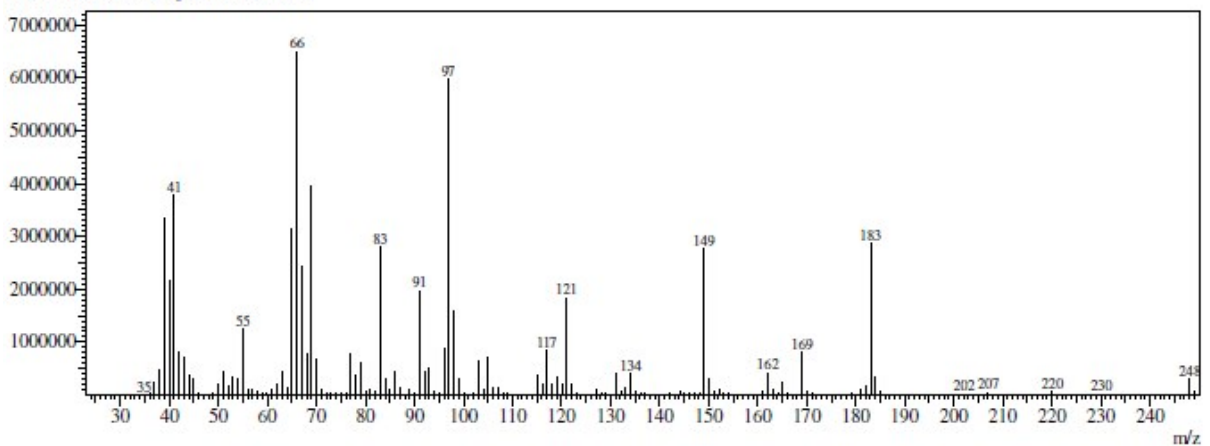
**Figure S6.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectra of P(N-HBO-MA) dried under vacuum for 24 h (bottom, A) and P(N-HBO-MA) dried under vacuum for 72 h (top, B)

➤ GC-MS data



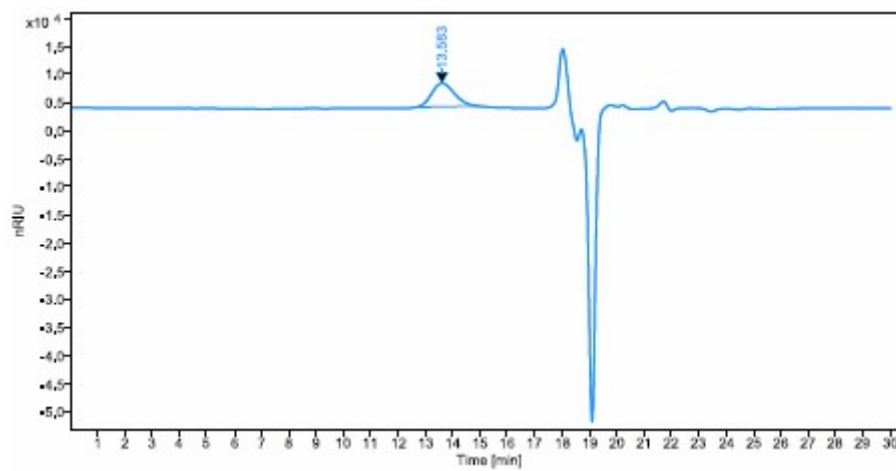
Spectrum

Line#:1 R.Time:10.875(Scan#:1186)  
MassPeaks:365  
RawMode:Single 10.875(1186) BasePeak:66.05(6498224)  
BG Mode:None Group 1 - Event 1 Scan

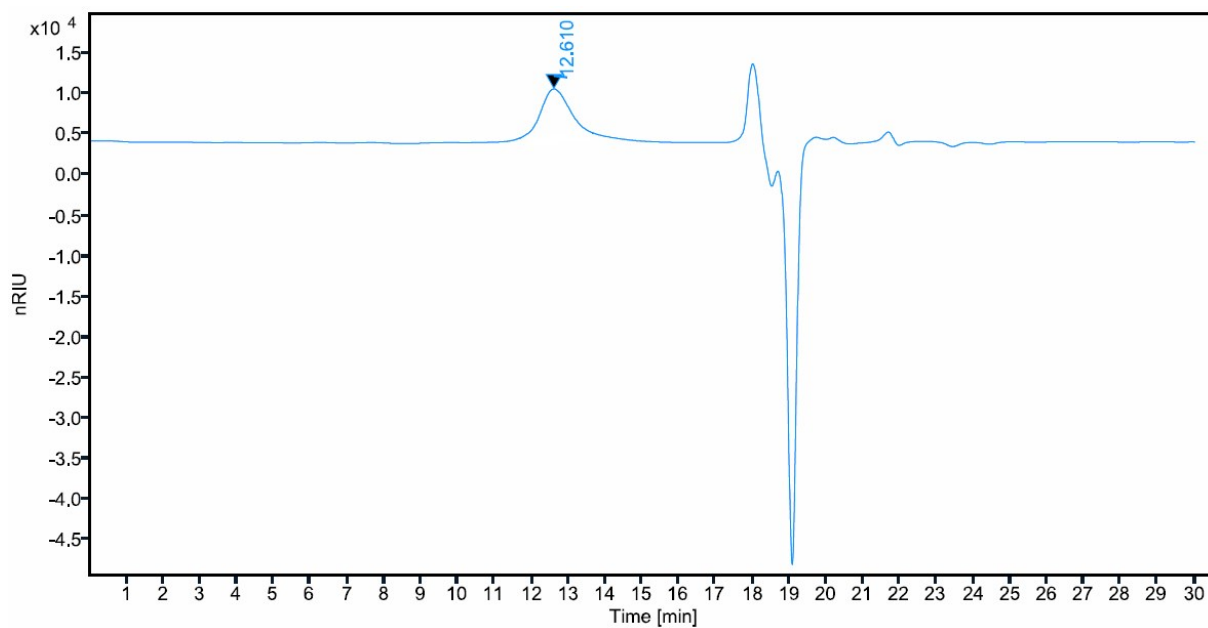


Figures S7. GC-MS chromatogram of N-HBO-MA

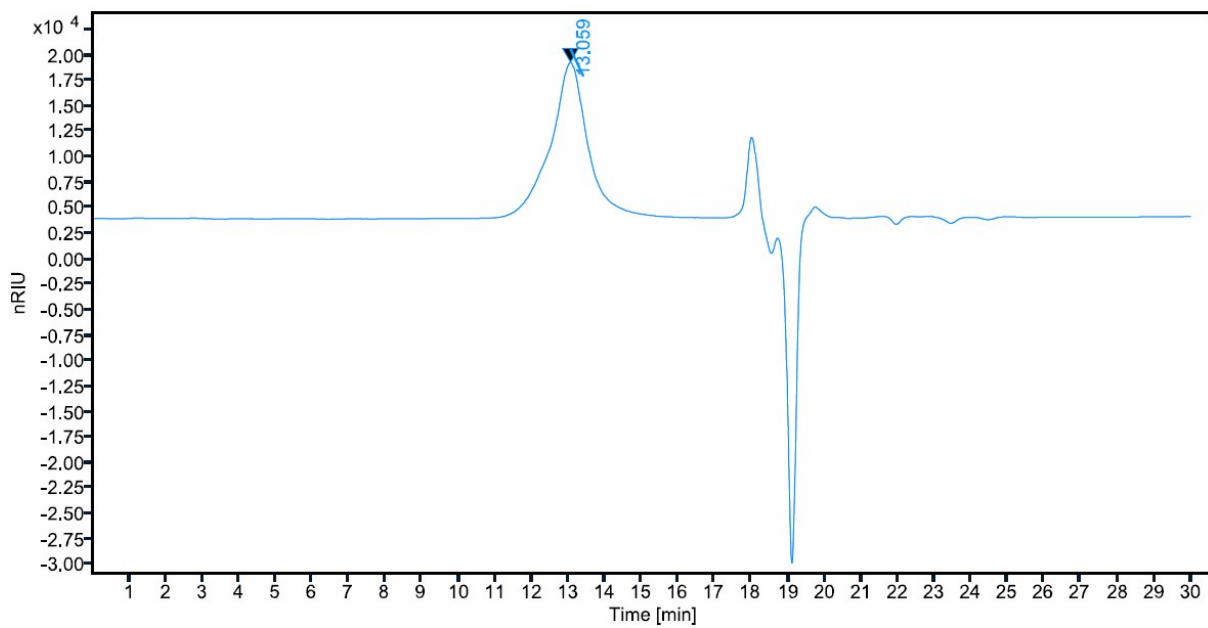
➤ SEC data



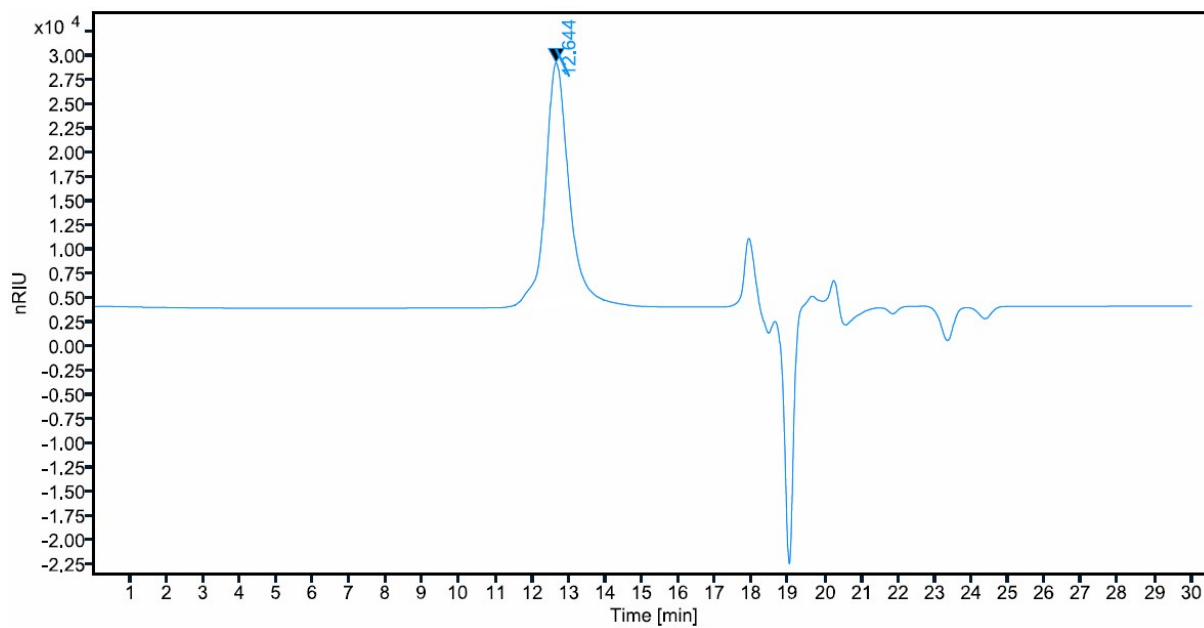
**Figure S8.** SEC trace of P(N-HBO-MA) prepared using C1 and 200 eq. of N-HBO-MA in DCM



**Figures S9.** SEC trace of P(N-HBO-MA) prepared using C2 (entry 1, Table 1)



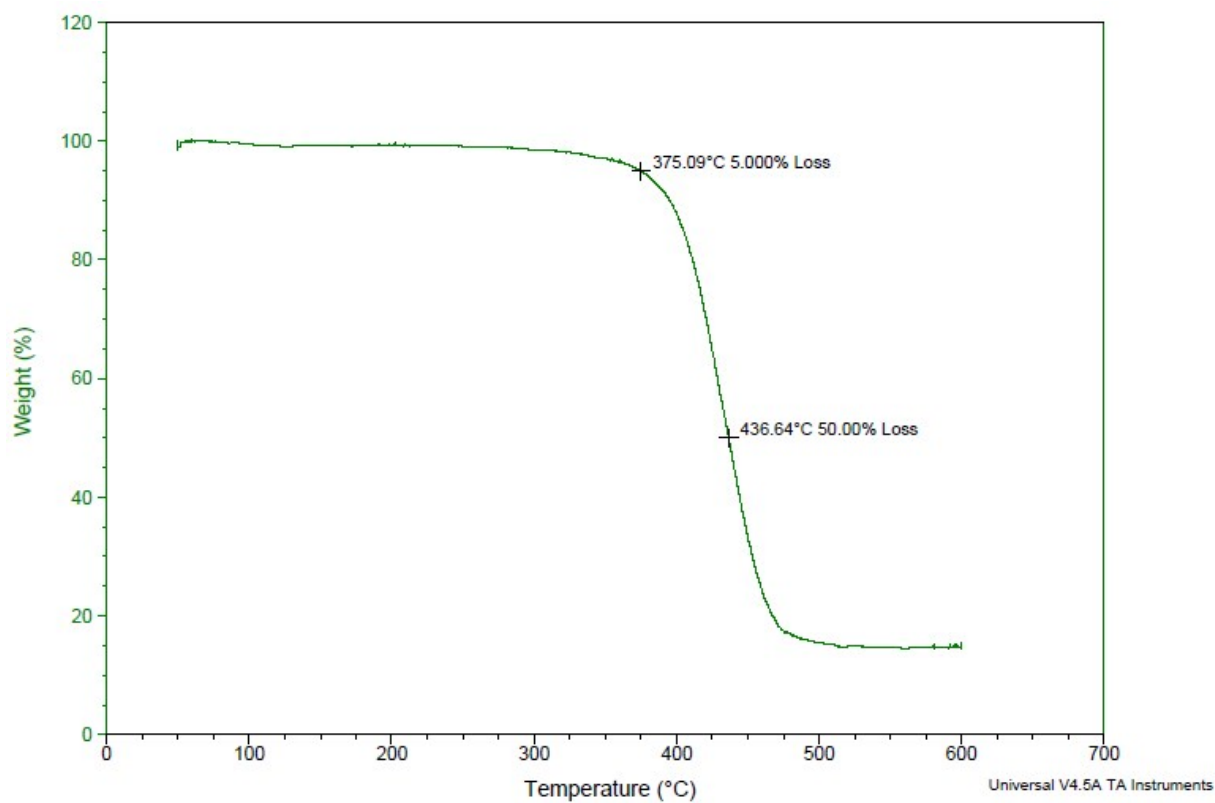
**Figures S10.** SEC trace of P(N-HBO-MA) prepared using C3 (entry 2, Table 1)



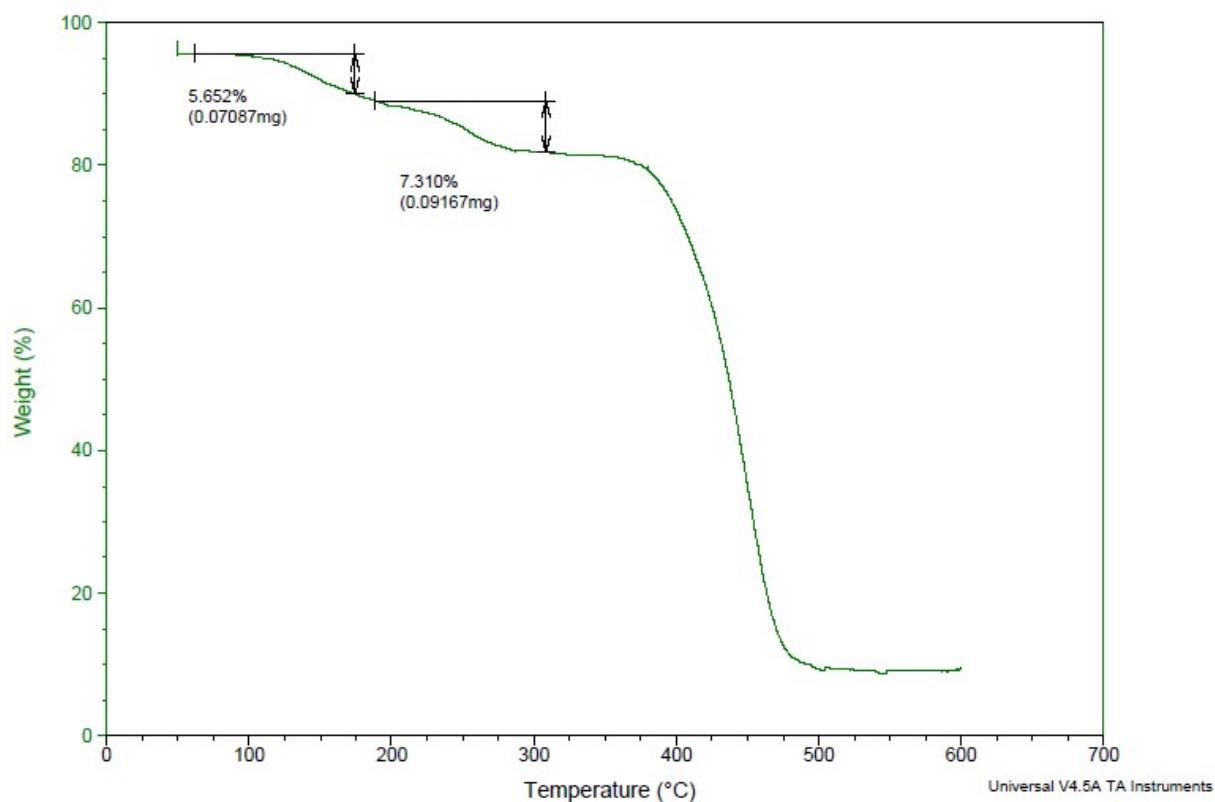
**Figures S11.** SEC trace of P(N-HBO-MA) prepared using C4 (entry 3, Table 1)



➤ TGA data



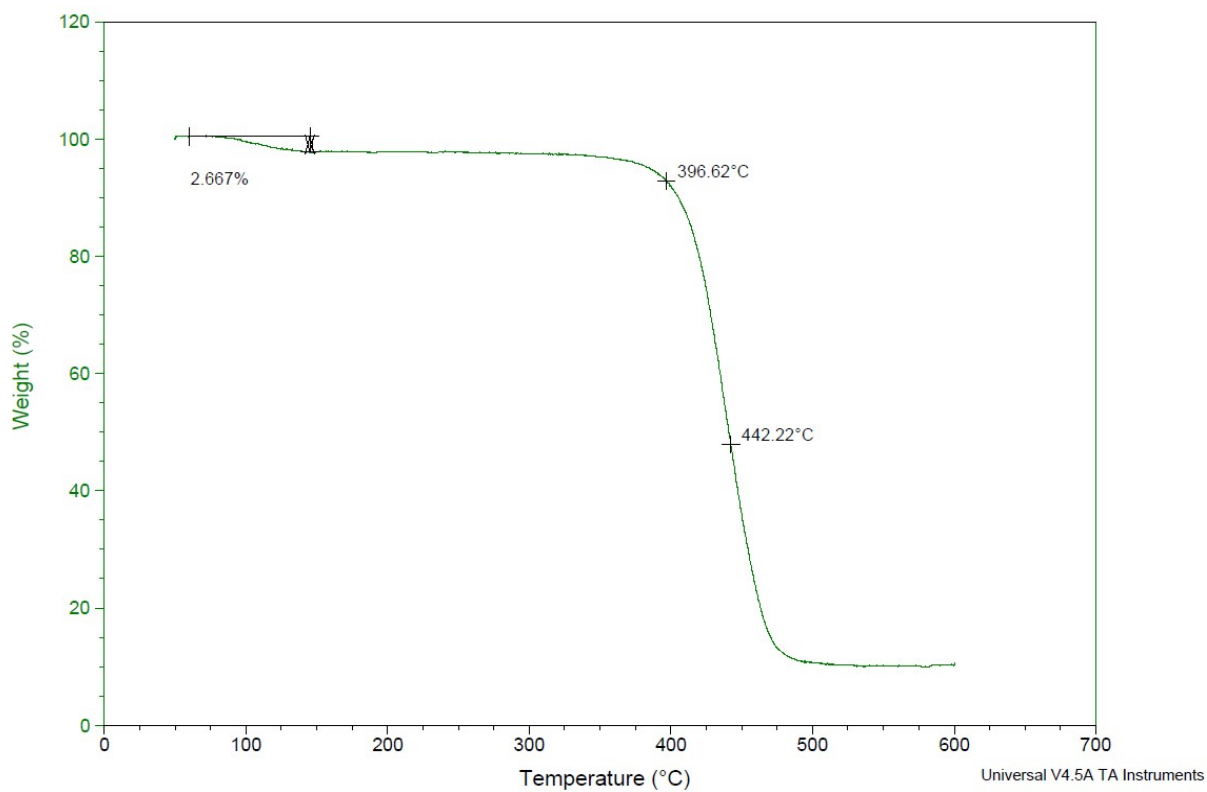
**Figure S12.** TGA trace of P(N-HBO-MA) prepared using C1 and 200 eq. of N-HBO-MA in DCM



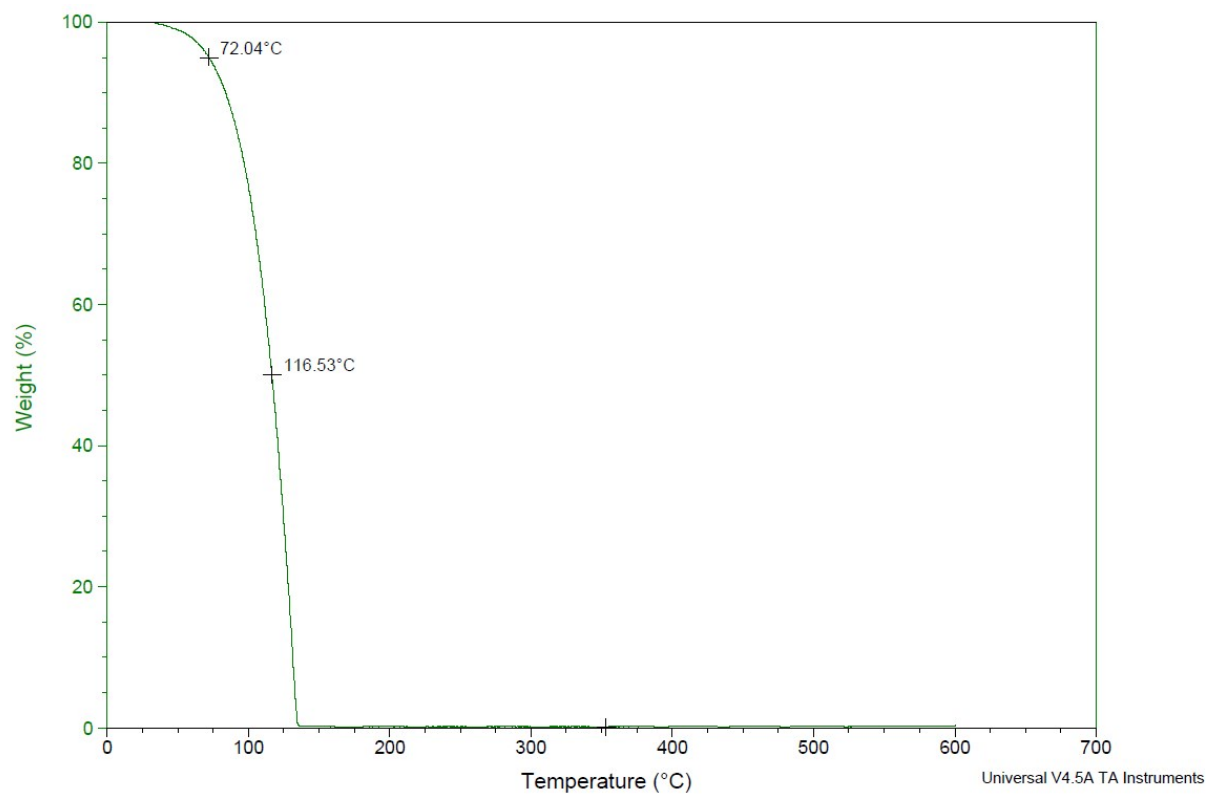
**Figure S13.** An example of a TGA trace of P(N-HBO-MA) prepared using C4 and in DCM



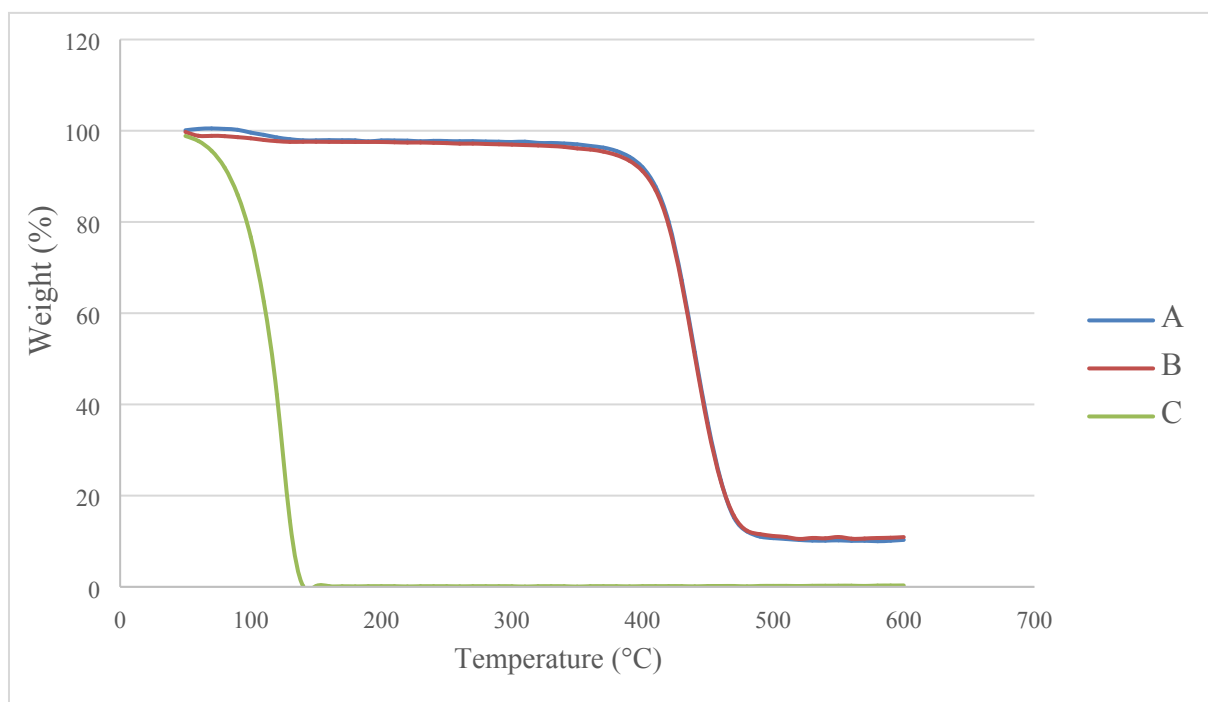
**Figures S14.** TGA trace of P(N-HBO-MA) dried for 72 h



**Figures S15.** TGA trace of P(N-HBO-MA) dried for 48 h

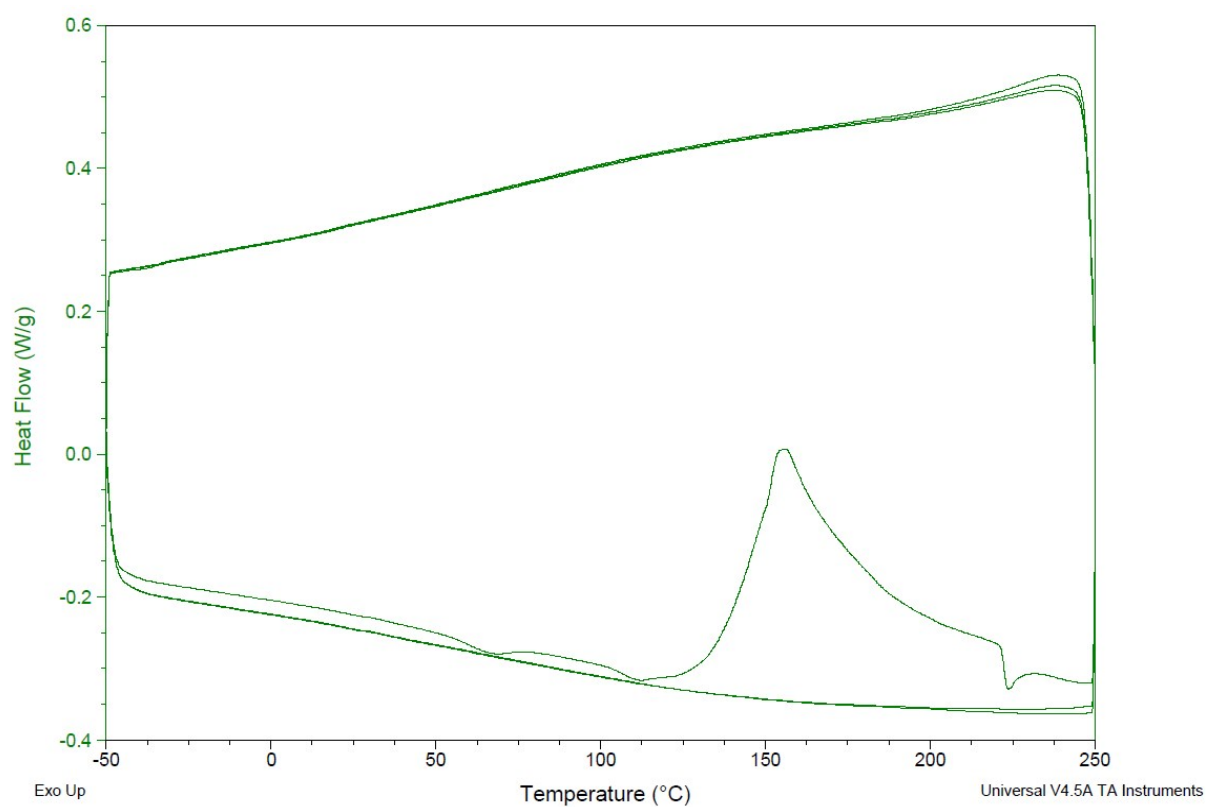


**Figures S16.** TGA trace of Cyrene™



**Figures S17.** TGA traces of P(N-HBO-MA) dried for 48 h and 72 h (A and B respectively) and Cyrene™ (C)

➤ DSC data



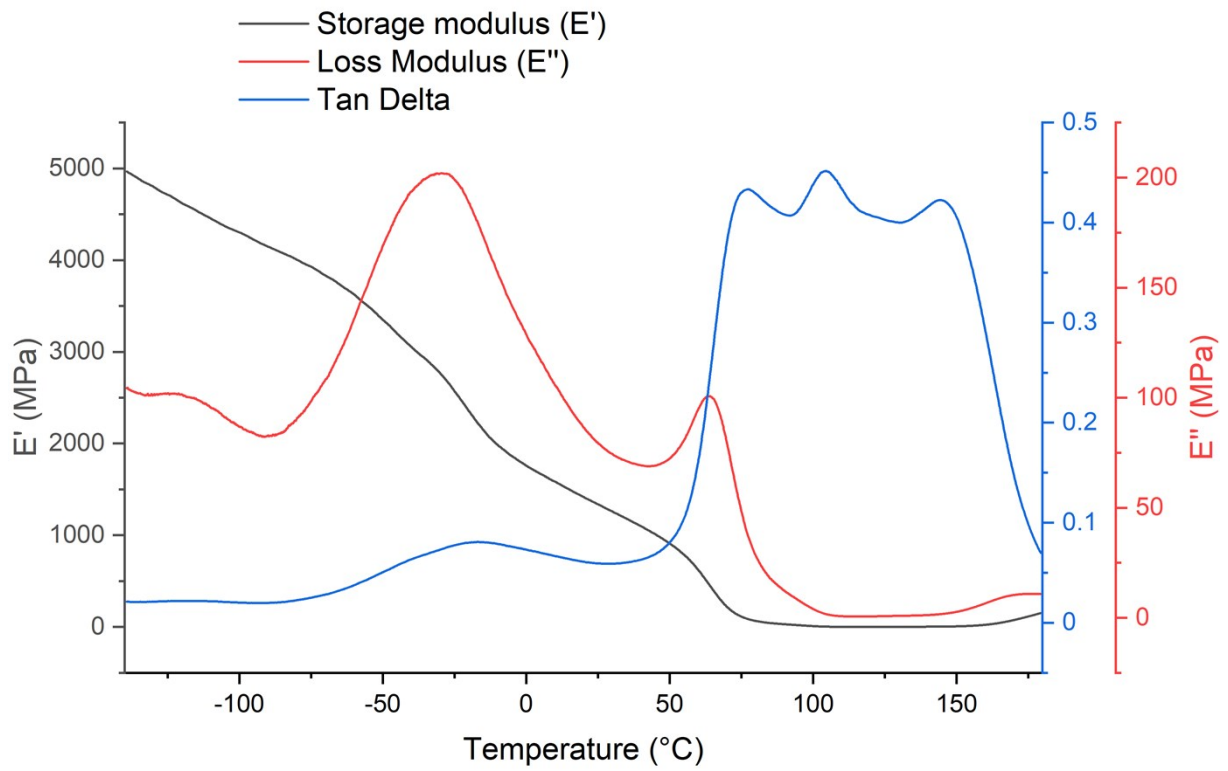
**Figure S18.** A typical DSC trace of P(N-HBO-MA) (entry 3, Table1) temperature ramp 10 °C/min from -50 to 250 °C

➤ **Polymer Film**



**Figure S19.** Polymer film of P(N-HBO-MA) prepared by solvent casting

➤ DMA



**Figure S20.** The variation of storage modulus, loss modulus and tan delta as a function of temperature of a P(N-HBO-MA) film recorded by DMA

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