Electronic Supplementary Information

Heterotelechelic Poly(propylene oxide) as Migration-Inhibited Toughening Agent in Hot Lithography Based Additive Manufacturing

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1. NMR Analyses of Synthesized Oligomers

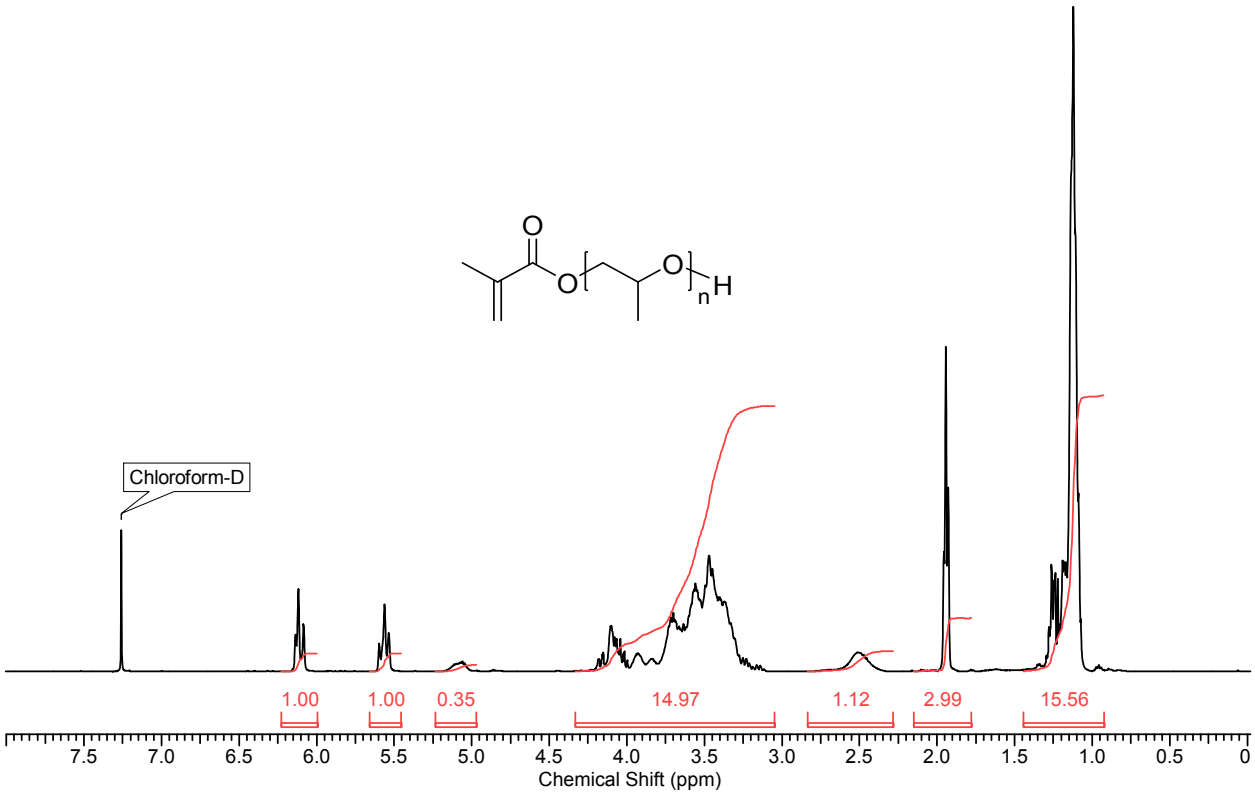

Figure S1: 400 MHz ^{1}H NMR spectrum of the starting material Bisomer PPM 5 LI.

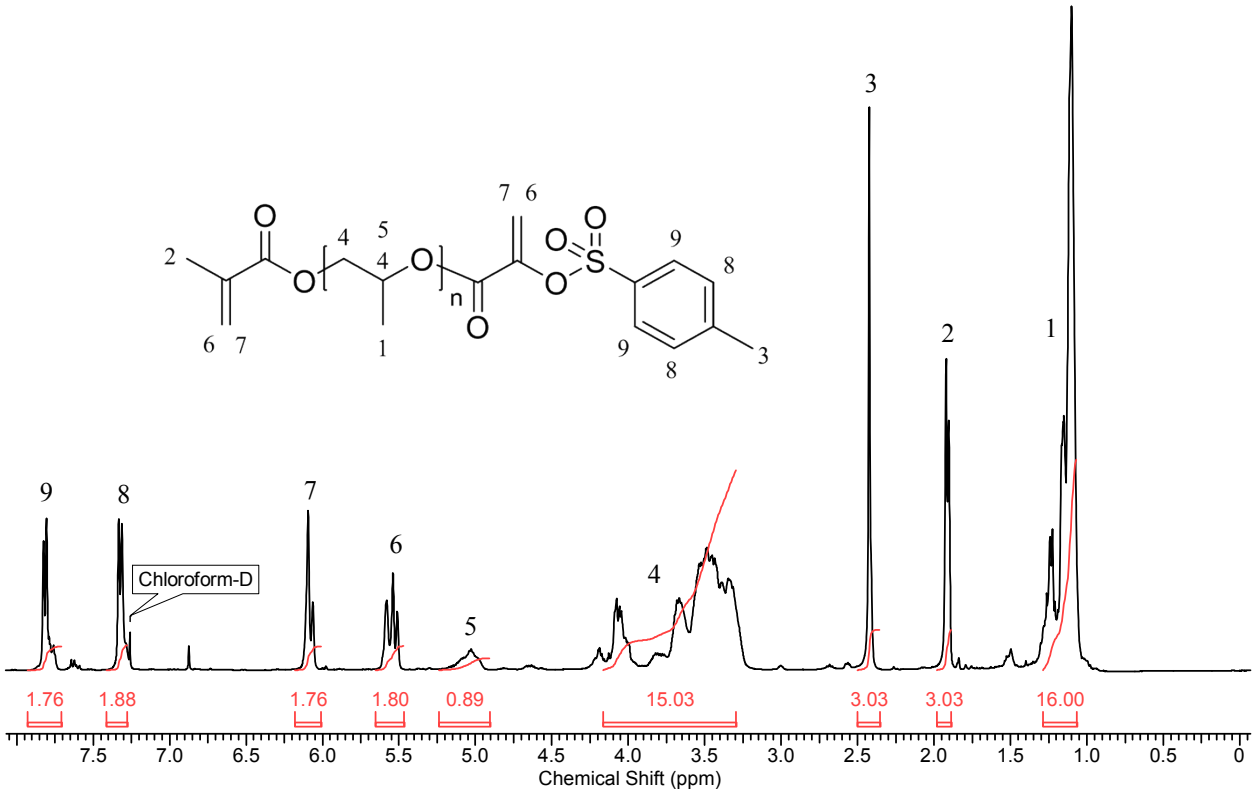

Figure S2: 400 MHz ^{1}H NMR spectrum of PPO Hybrid (PPO-H).

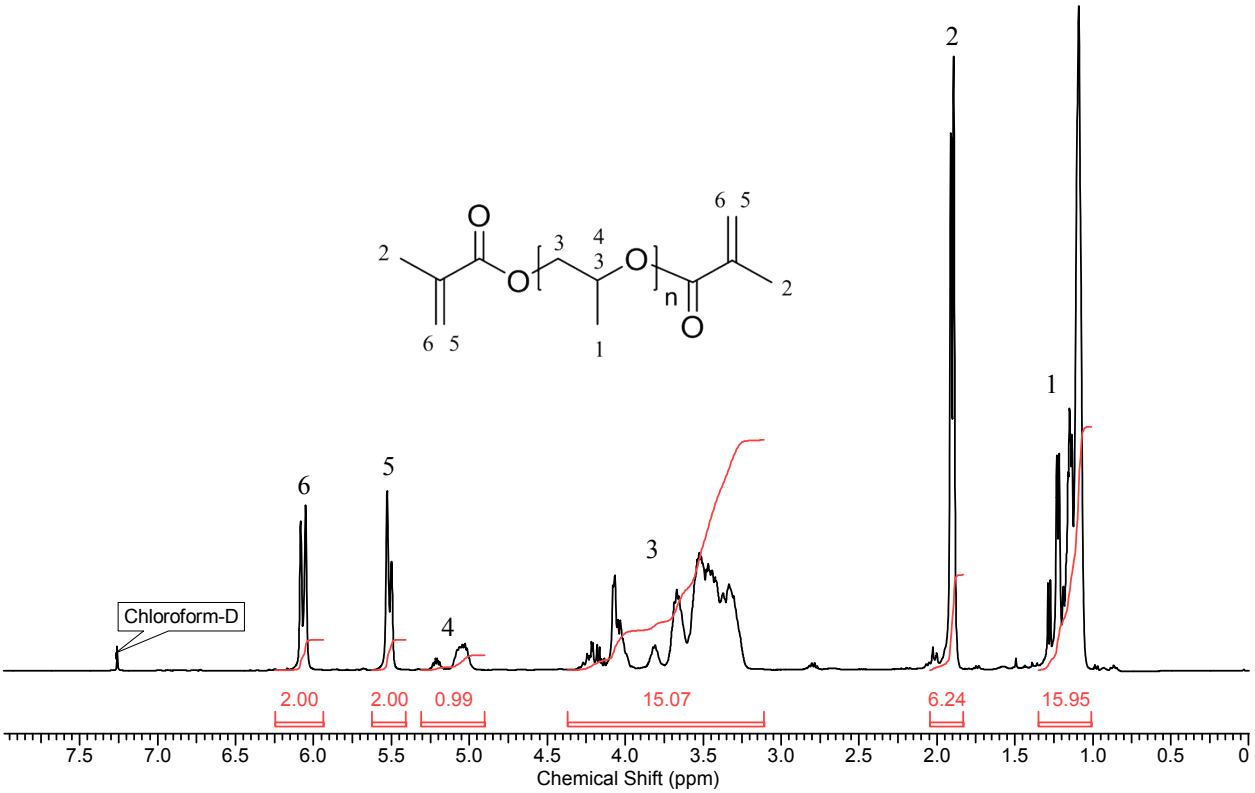

Figure S3: 400 MHz ^{1}H NMR spectrum of PPO Dimethacrylate (PPO-D).

2. Side Reaction of Tosyl Chloride and Hydrochinone

Previous experiments showed that for the synthesis of PPO-H, concentrated sulfuric acid was the most efficient transesterification catalyst. However, 3 wt% of hydrochinone had to be used in order to prevent premature polymerization. As the hydrochinone was hard to remove after the first reaction step, 1,4-Phenylene bis(4-methylbenzenesulfonate) was formed as a side product during the second reaction step. Most of the side product could be removed during workup. Nevertheless, traces can still be seen in the ^{1}H NMR spectrum of PPO-H.

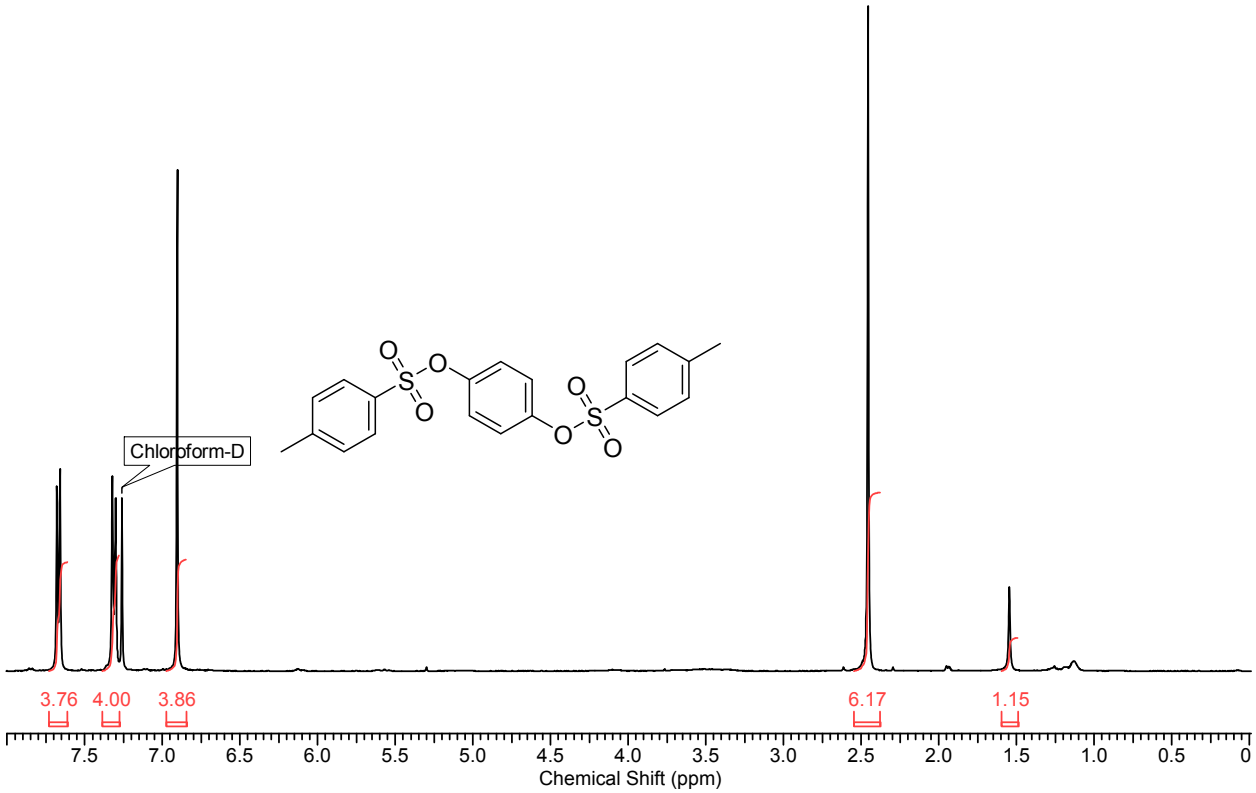

Figure S4: 400 MHz ^{1}H NMR spectrum of 1,4-Phenylene bis(4-methylbenzenesulfonate) as the side product during PPO-H synthesis.

3. DMTA, Tensile Testing, Dynstat, and Swelling Data

In the following table, data obtained from DMTA, tensile tests, dynstat experiments, and swelling experiments discussed and depicted in Figures 2-5 and 7-10 in the paper are given. Figure S5 displays representative stress-strain curves of all discussed materials.

Table S1: Thermomechanical characteristics for moulded and 3D printed specimens made from pure Bomar and Bomar with 10 - 25 db% poly(propylene oxide) dimethacrylate (PPO-D) or poly(propylene oxide) hybrid monomer (PPO-H): DMTA results (glass transition temperature (T_g), storage moduli at 25 °C (G'_{25}, as a measure for the onset of storage modulus decrease) and at the rubber plateau (G'_{rubber})); tensile testing results (ultimate tensile stress (σ_M), strain at break (ε_B), and energy at break (E_B, calculated from the area under the stress-strain curve)); impact strength (a) obtained from dynstat measurements; : swellability (S) and gel fraction (G)

Formulation	T_g / °C [1]	G'_{25} / Pa [2]	G'_{rubber} / Pa [3]	σ_M [MPa]	ε_B [%]	E_B [MJ m^{-3}]	a [kJ m^{-2}]	S [%]	G [%]
Bomar	109	$1.79\cdot10^9$	$1.30\cdot10^7$	76.0 ± 2.2	14.3 ± 4.2	8.1 ± 2.7	12.7 ± 4.1	123[4]	100[4]
PPO-D "10 %"	102	$1.56\cdot10^9$	$1.36\cdot10^7$	70.9 ± 2.3	17.3 ± 6.3	9.5 ± 3.8	14.5 ± 3.1	123 ± 1	100[4]
PPO-D "15 %"	101	$1.53\cdot10^9$	$1.54\cdot10^7$	66.8 ± 2.6	19.2 ± 7.6	9.2 ± 3.9	14.4 ± 5.0	122[4]	99[4]
PPO-D "20 %"	101	$1.42\cdot10^9$	$1.73\cdot10^7$	61.0 ± 2.2	17.7 ± 5.1	8.6 ± 2.9	15.3 ± 3.2	121[4]	99[4]
PPO-D "25 %"	99	$1.15\cdot10^9$	$1.70\cdot10^7$	55.5 ± 3.2	14.7 ± 6.6	6.6 ± 3.5	15.2 ± 1.4	120 ± 1	99[4]
PPO-H 10 %	86	$1.50\cdot10^9$	$7.85\cdot10^6$	63.0 ± 1.6	32 ± 17	15.1 ± 7.8	19.7 ± 3.7	130 ± 1	98[4]
PPO-H 10 % 3D	88	$1.52\cdot10^9$	$8.94\cdot10^6$	59.0 ± 1.2	20.2 ± 5.1	9.0 ± 2.2	7.8 ± 1.0	126 ± 1	99[4]
PPO-H 15 %	76	$1.33\cdot10^9$	$6.52\cdot10^6$	54.1 ± 1.6	54 ± 18	21.5 ± 7.5	24.4 ± 2.2	133[4]	97[4]
PPO-H 15 % 3D	78	$1.39\cdot10^9$	$7.47\cdot10^6$	50.5 ± 0.9	38 ± 17	14.1 ± 6.8	11.8 ± 4.1	128[4]	99[4]
PPO-H 20 %	66	$1.10\cdot10^9$	$5.35\cdot10^6$	43.0 ± 2.9	84 ± 14	30.0 ± 6.3	28.2 ± 2.1	139 ± 1	94 ± 1
PPO-H 25 %	55	$7.48\cdot10^9$	$4.05\cdot10^6$	34.7 ± 4.7	112 ± 16	29.2 ± 5.7	47.4 ± 6.1	154 ± 3	87 ± 2

[1] determined from the maximum of the loss factor curve

[2] first G' value at/after 25.0°C

[3] mean of all G' values between 141 and 200 °C

[4] deviation of triplicates < 0.5%

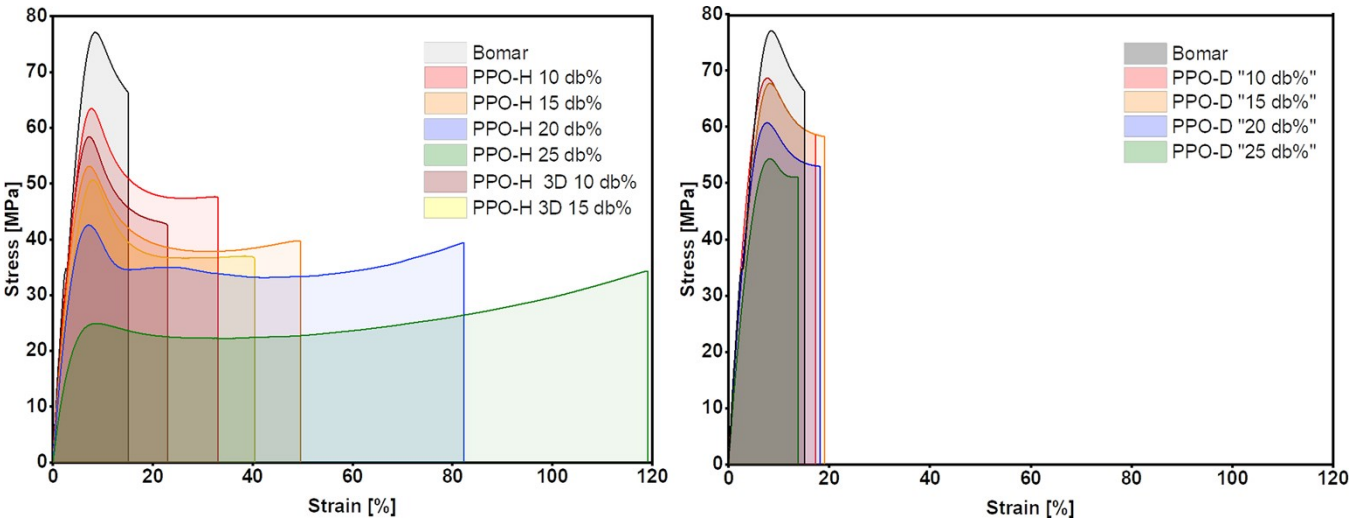

Figure S5: Representative stress-strain curves of PPO-H containing testing specimens (left) and PPO-D containing testing specimens (right) compared to only Bomar-containing testing specimens

4. Image of the Printed Specimens for DMTA, Tensile Testing, and Dynstat

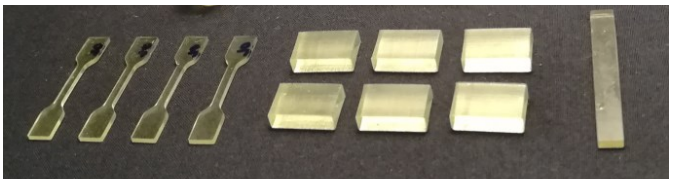

Figure S6: Image of the 3D-printed specimens for tensile testing (left), dynstat testing (middle), and DMTA (right)