Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

Photo-chemically induced polycondensation of a pure phenolic resin for additive manufacturing

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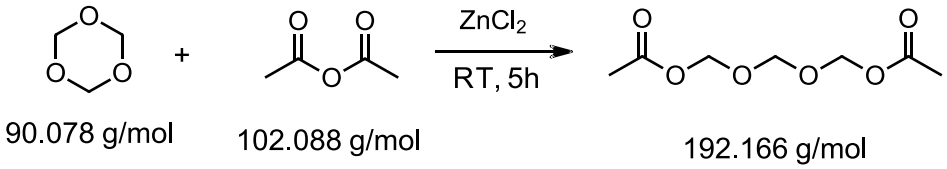
Experimental Part

Synthesis of trioxymethylene-diacetate (TOMDA)



The synthesis of TOMDA was performed in accordance with the literature.[1] n-Trioxane (22.50 g, 250 mmol, 1 eq.) was mixed with freshly distilled acetic anhydride (25.55 g, 250 mmol, 1 eq.) and stirred with $ZnCl_2$ (1.02 g, 7.5 mmol) at 25 °C for 5 h. The mixture was washed with saturated $NaHCO_3$ solution followed by extraction with diethyl ether (3 x 200 mL). The organic phase was dried over Na_2CO_3. The solvent was evaporated and the crude product was purified by subsequent distillation to obtain the product as a clear liquid (40.12 g, 84 %).

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm): 5.36-5.33 (m, 4H, CH_2 oxymethylen-1); 4.93-4.87 (m, 2H, CH_2 oxymethylen-2); 2.10-2.09 (m, 6H, CH_3)

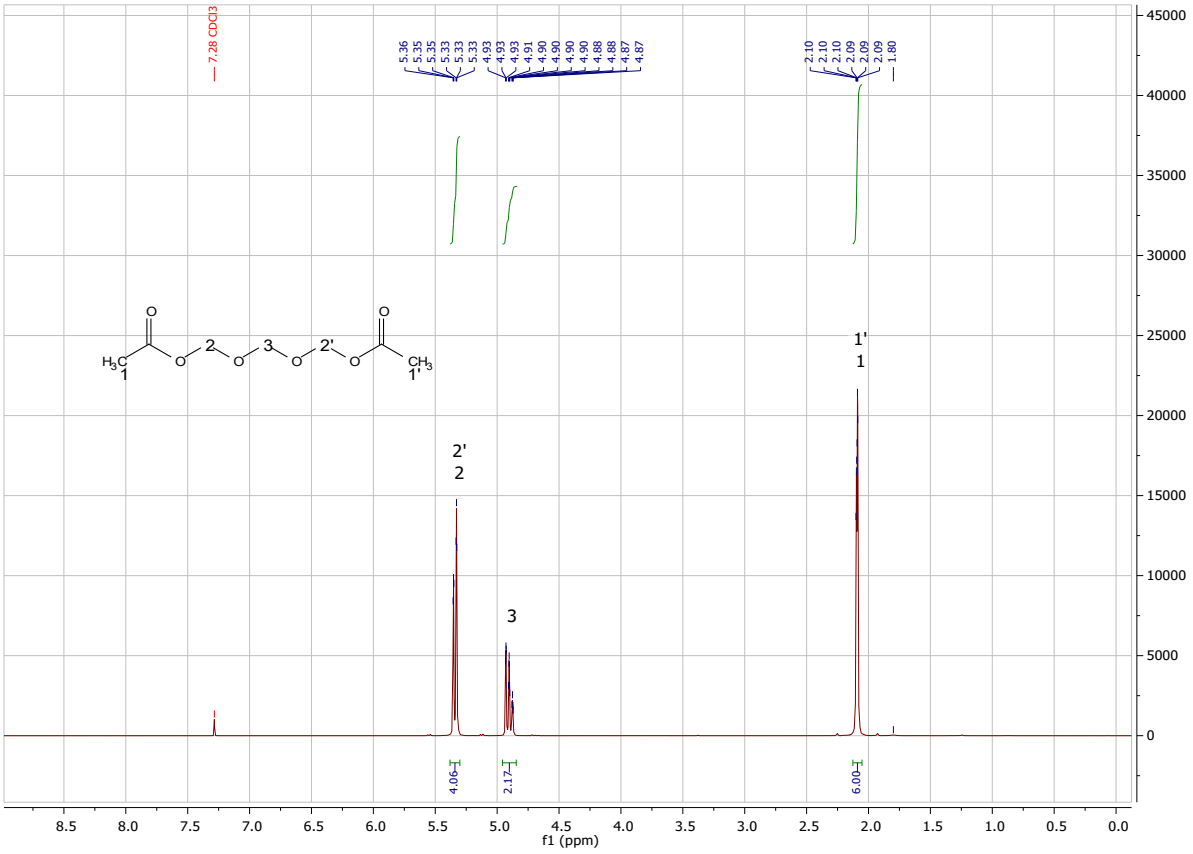


Figure S1: ^{1}H-NMR of TOMDA ($CDCl_3$, 400 MHz) δ: 5.36-5.33 (m, 4H), 4.93-4.87 (m, 2H), 2.10-2.09 (m, 6H)

Photo-DSC

Table S1: Results of the photo-DSC experiments of the PF and TOMDA formulations.

CA	*Temp. [°C]*	*$_{\Delta}H$ [Jg^{-1}]*	*T_{max} [s]*
PF	60	145 ± 10	20 ± 1
	80	240 ± 10	13 ± 1
	90	240 ± 10	10 ± 1
	100	160 ± 10	8 ± 1
	120	120 ± 10	8 ± 1
TOMDA	80	360 ± 10	14 ± 1
	90	360 ± 10	10 ± 1
	100	345 ± 10	9 ± 1
	120	180 ± 20	5 ± 1

Microscopy of 3D printed object

The 3D printed objects were investigated by light microscopy. For that, the samples were prepared from rectangular specimens by grinding and polishing, which was done manually on rotating plates. The overview to observe macroscopic voids was recorded by a Keyence VHX 6000 optical microscope in panorama mode.

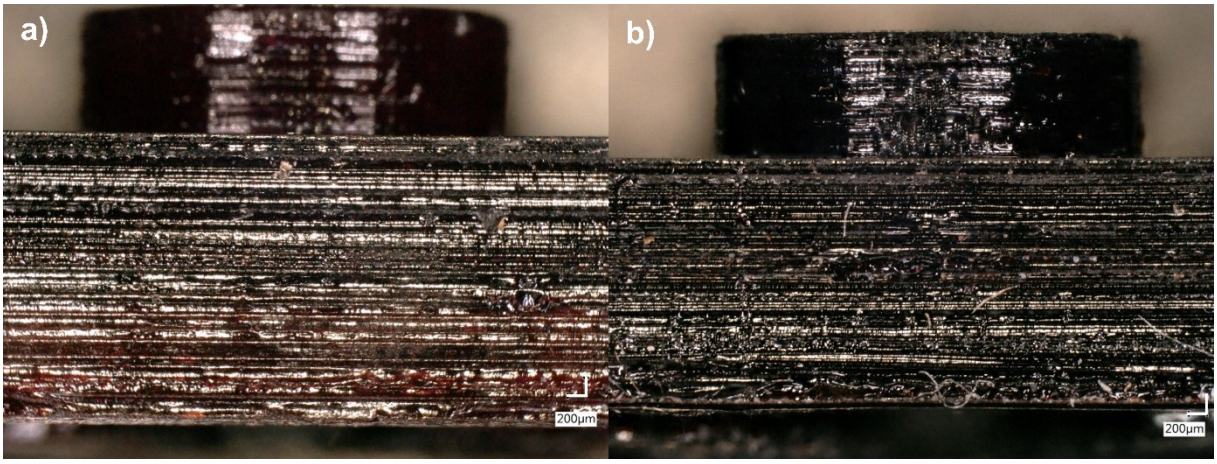


Figure S2: Microscopic image of the 3D printed object (a) before and (b) after the post-curing process.

Tensile Tests

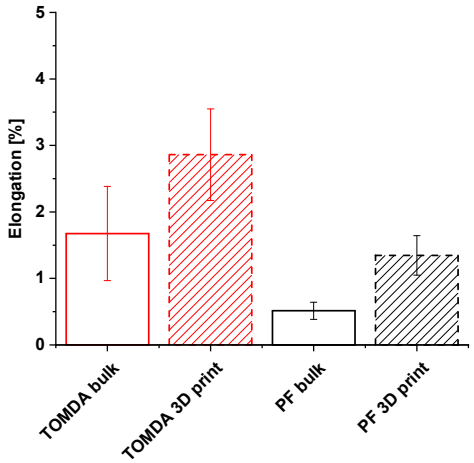


Figure S3: Elongation at break of bulk cured and 3D printed parts.