Supplementary information

Exploration of post-print modification of 3D photo-printed materials for microfabrication by means of RAFT polymerization

For the surface modification resist, a PETA was introduced in the CDTPA raft agent by reacting a single acrylate with the chain transfer agent under blue light irradiation. The experimental details are described under 'PETA insertion in CDTPA RAFT agent'. Figure S1 shows the reaction scheme, a series of NMR spectra containing the samples of reaction progress. The conversion of virgin CDTPA was calculated by the relative integration of the methyl group peak, which moves from 1.9 ppm to a split around 1.4 ppm.

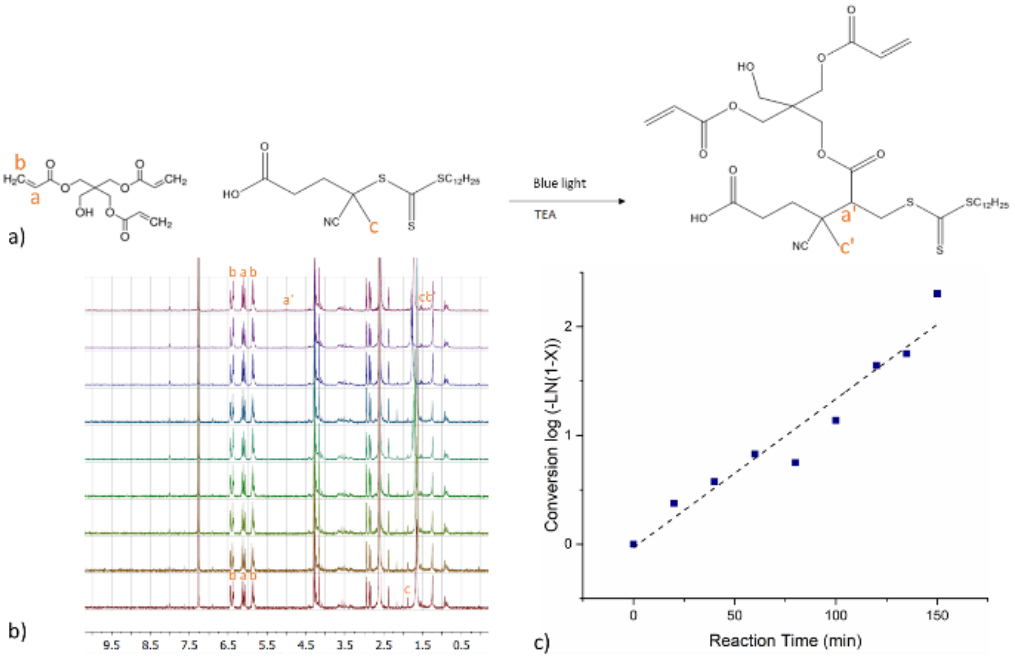

Figure S1 a) Scheme of PETA introduction into CDTPA using a precursor reaction. b) ^{1}H-NMR spectrum sampling during the precursor reaction with PETA:CDTPA ratio 1:12.5. The methyl peak changes position when an acrylate is introduced. c) based on the relative size of the methyl peak at 1.9 ppm compared to the start, the conversion of virgin CDTPA was calculated and displayed in a logarithmic scale over time and follows first order kinetics.

The size of the acrylate peaks should also decrease as the PETA reacts with CDTPA, but with the 1:12.5 CDTPA:PETA ratio, the relative change was too small for an accurate conversion graph. Therefore, the reaction was repeated in the exact conditions described in the experimental section, except for the ratio between chain transfer agent and monomer, which we reduced to 1:5.3. The results are presented in
Figure S2 which initially follow first order kinetics, but start deviating after 2 hours slowing down slightly. At this point, virgin CDTPA starts to deplete meaning the secondary monomer introduction becomes the dominant reaction. This has a different rate explaining the change in slope. However, the acrylate conversion of over 20% suggests that 3-4 acrylates per CDTPA agent have reacted. Despite the multi-monomer reaction, the product was still a viscous liked and furthermore soluble in solvents like ethanol and 2-propanol used for development of TPP samples. This made it suitable for the purpose as a resist for microstructure fabrication.

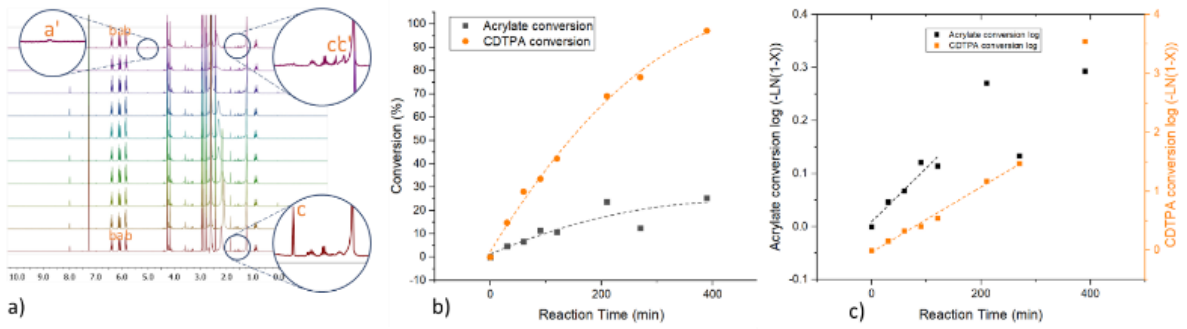

Figure S2. a) ^{1}H-NMR spectrum sampling during the precursor reaction with PETA:CDTPA ratio 1:5.3. b) based on the relative sizes of the acrylate groups compared to the start the PETA conversion was calculated and similarly the CDTPA conversion based on relative methyl peak size at 1.9 ppm. Here the conversion is displayed as a percentage of the original concentration of the acrylates (in case of PETA therefore not the molecules). c) The conversion is displayed in log scale which seems to have consistent first-order kinetics until the final data point, which could indicate the end of the precursor reaction and change toward dominance of the multi-acrylate insertion reaction.

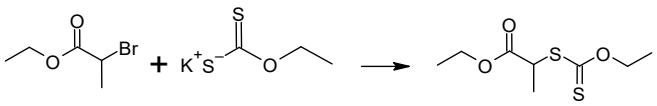

Figure S3. Reaction scheme of (S)-2-(Ethyl propionate)-(O-ethyl xanthate) (EPEX). Based on work of [45]

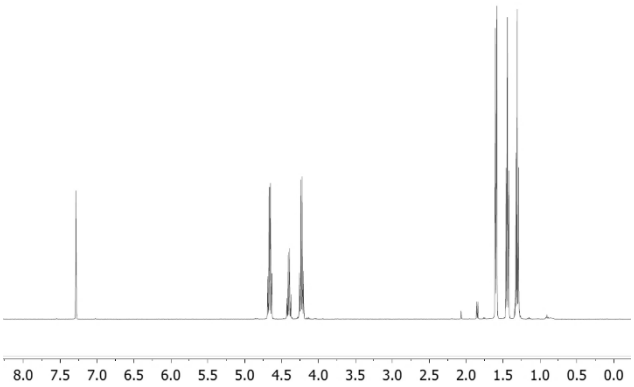

Figure S4 The ^{1}H-NMR spectrum of EPEX

Analysis of the spectrum of EPEX. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (q, 2H, C(S)OC***H₂***), 4.40 (q, 1H, C***H***), 4.23 (q, 2H, C(O)OC***H₂***), 1.59 (d, 3H, C***H₃***CH), 1.44 (t, 3H, C(S)OCH$_2$C***H₃***), 1.31 (t, 3H, C(O)OCH$_2$C***H₃***).

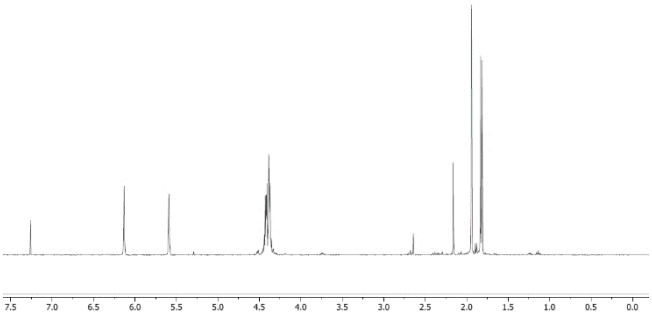

Figure S5: ^{1}H-NMR spectrum after the first step 1 of the tetra-functional xanthate.

Analysis of the spectrum of the intermediate product, reaction scheme in Error! Reference source not found.**A.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (q, *J* = 1.2 Hz, 1H, C(H)***H***C), 5.59 (h, *J* = 1.5 Hz, 1H, C(H)***H***C), 4.55 – 4.27 (m, 5H, C***H₂***C***H₂***OC(O)C***H***), 1.94 (q, *J* = 1.1 Hz, 3H, CH_2CC***H₃***), 1.82 (dd, *J* = 6.9, 0.9 Hz, 3H, C(Br)C***H₃***).

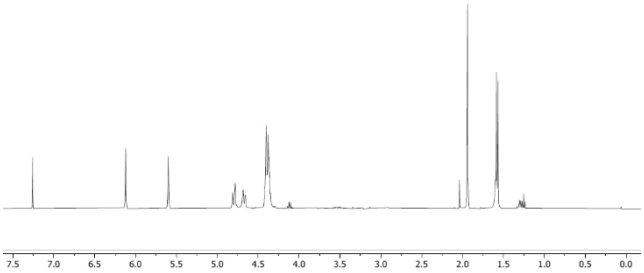

Figure S6: ^{1}H-NMR spectrum of the tetra-functional xanthate.

Analysis of the spectrum of the final product, reaction scheme in Error! Reference source not found.**A.** ^{1}H NMR (400 MHz, cdcl$_3$) δ 6.12 (s, 4H, 4x C(H)***H***C), 5.60 (s, 4H, 4x C(H)***H***C), 4.74 (q, *J* = 8H, 4x C(C***H₂***O)$_4$), 4.46 – 4.25 (m, 20H, 4x C***H₂***C***H₂***OC(O)C***H***), 1.94 (t, *J* = 1.2 Hz, 12H, 4x CH_2CC***H₃***), 1.58 (d, *J* = 7.4 Hz, 12H, 4x C(S)C***H₃***).

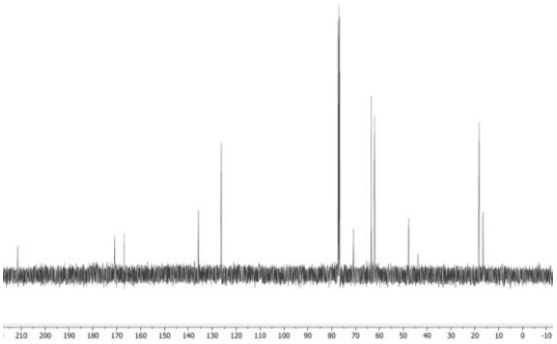

Figure S7 ^{13}C-NMR spectrum of the tetra-functional xanthate.

Analysis of the spectrum of the final product, reaction scheme in Error! Reference source not found.**A.** ^{13}C NMR (101 MHz, $CDCl_3$) δ (211.51, O***C***(S)S), 170.90 (SC(CH_3)***C***(O)O), 166.97 ($CH_2C(CH_3)$***C***(O)O), 135.83 (CH_2***C***(CH_3)C(O)O), 126.22 (***C***$H_2C(CH_3)C(O)O$), 70.87 (C(***C***$H_2O)_4$), 63.46 ($CH_2C(CH_3)C(O)O$***C***H_2CH_2), 62.02 ($CH_2C(CH_3)C(O)O$***C***H_2CH_2), 47.81 (S***C***(CH_3)C(O)O), 43.79 (***C***$(CH_2O)_4$), 18.28 (CH_2C(***C***H_3)), 16.70 (SC(***C***H_3)).