Supporting Information

Investigation of design of macromolecular-based inks on material properties for two-photon 3D laser printing

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Outline

1. Materials

The following chemicals were used as received unless otherwise indicated. All monomers were filtered over basic Al_2O_3 prior to use. 2,2′-azobis(2-methylpropionitrile) was recrystallized from methanol prior to use. 1,4-dioxane (≥99%, Fisher Scientific); 2-cyano-2-propyl dodecyl trithiocarbonate (97%, BLDpharm), 2-hydroxyethyl acrylate (96%, Sigma-Aldrich); acetone (technical grade, Fisher Scientific); acetonitrile (99.9%, Fisher Scientific); acryloyl chloride (≥97.0%, Sigma-Aldrich); Al_2O_3 (activated basic, Sigma Aldrich), Al_2O_3 (activated neutral, Sigma Aldrich), 2,2′-azobis(2-methylpropionitrile) (98%, Sigma Aldrich), butyl acrylate (≥99.0%, Sigma-Aldrich); chloroform (dry, 99.9%, Fisher Scientific); chloroform (≥99%, Fisher Scientific); chloroform-d (99.8 atom % D, Fisher Scientific); dichloromethane (dry, 99.8%, Fisher Scientific); dichloromethane (≥99%, Fisher Scientific); n-hexane (≥99%, Sigma Aldrich) $MgSO_4$ (≥98.0%, Fisher Scientific); $NaHCO_3$ (99%, Grüssing GmbH); toluene (≥99.7%, Fisher Scientific).

2. Synthesis of Polymers: X-co-HEA

For a typical RAFT polymerization the following feed ratios of comonomers X:HEA were used: BA:HEA (6:4 eq.), IBA:HEA (10:6) and MA:HEA (8:6 eq.). Monomers were combined with and 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (342.7 mg, 1 µmol, 1.0 eq.) and dissolved in toluene (8 mL). The mixture was transferred to a Schlenk tube and AIBN (8.1 mg, 0.05 mmol, 0.05 eq.) was added. The solution was degassed through freeze-pump-thaw (4 x 8 min), followed by backfilling with nitrogen. The reaction mixture was stirred at 100 °C for 35 min. The reaction was quenched by immersion in liquid nitrogen and opened to atmosphere. After dilution with DCM, the solution was precipitated into cold n-hexane. After centrifugation and decanting of the supernatant, the copolymer X-co-HEA was received as a yellow solid.

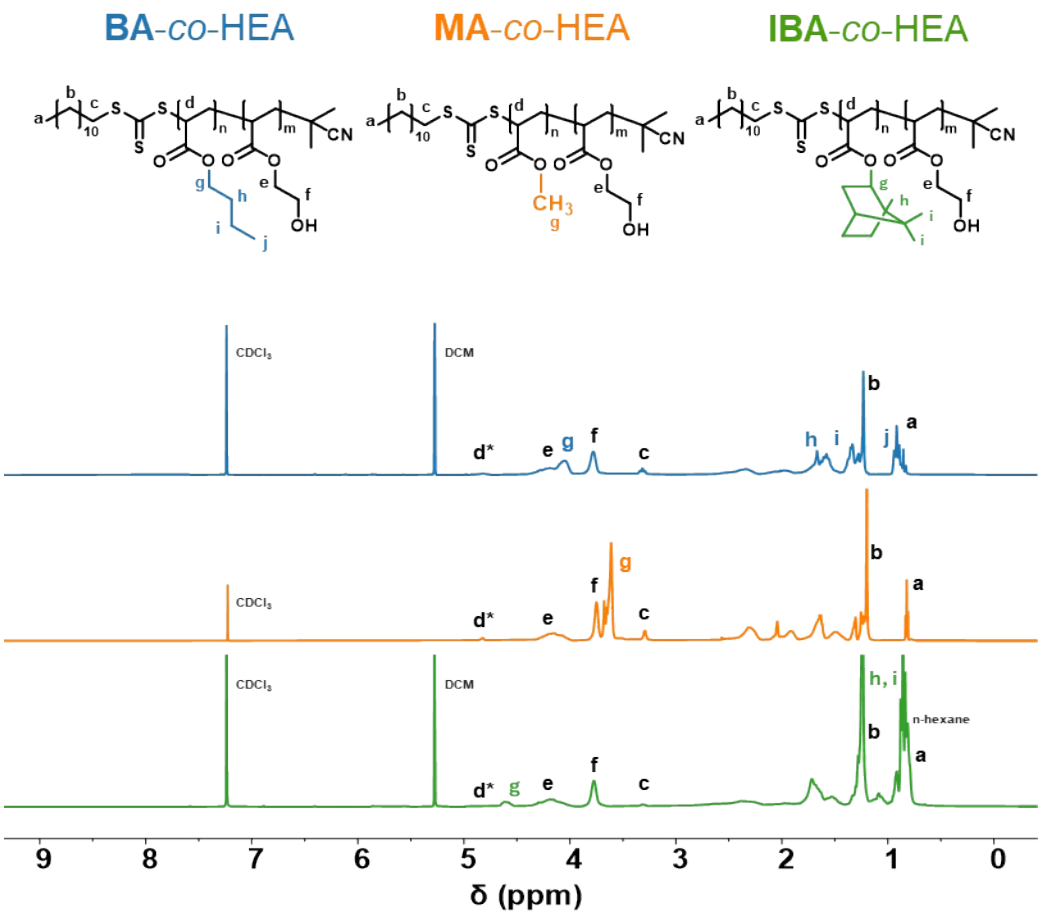

Figure S1: ^{1}H-NMR spectra ($CDCl_3$, 600 MHz, 16s, 295 K) of X-co-HEA: BA-co-HEA (top, blue), MA-co-HEA (middle, orange) and IBA-co-HEA (bottom, green).

3. Post-Functionalization with Acryloyl Chloride: X-co-Acryl

For a typical post-functionalization reaction the following procedure was followed: under a nitrogen atmosphere, non-functionalized polymer (X-co-HEA, 150.0 mg, 1 eq. OH) was dissolved in dry DCM (20 mL). Et_3N (3 eq.) was added to the solution under nitrogen and stirred for a few minutes. The solution was cooled in ice and to this, acryloyl chloride (3.5 eq) was added dropwise. The mixture was allowed to reach room temperature overnight under nitrogen atmosphere. The solvent was evaporated and the crude mixture redissolved in acetonitrile (30 mL) and 5% $NaHCO_3$ (30 mL). The solution was extracted with DCM (3 x 30mL). The organic fraction was dried over $MgSO_4$, filtered, and concentrated under reduced pressure, taking care not to heat above 40 °C. The product was then precipitated from DCM into ice cold n-hexane. After centrifugation the pellet was dried and the product was obtained as a yellow solid (typical yield approx. 100 mg, 67%).

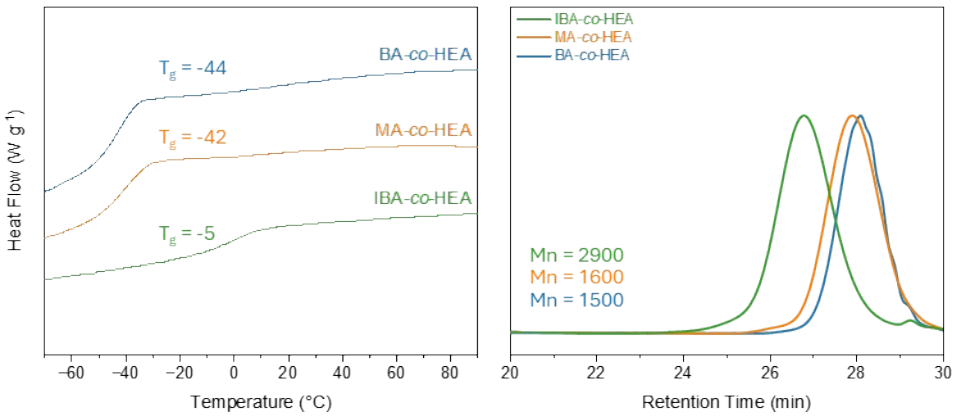

Figure S2: left) DSC profiles and right) SEC chromatograms of the three pre-polymers, BA-co-HEA (blue), MA-co-HEA (orange), and IBA-co-HEA (green).

4. FT-IR Microscopy Characterization

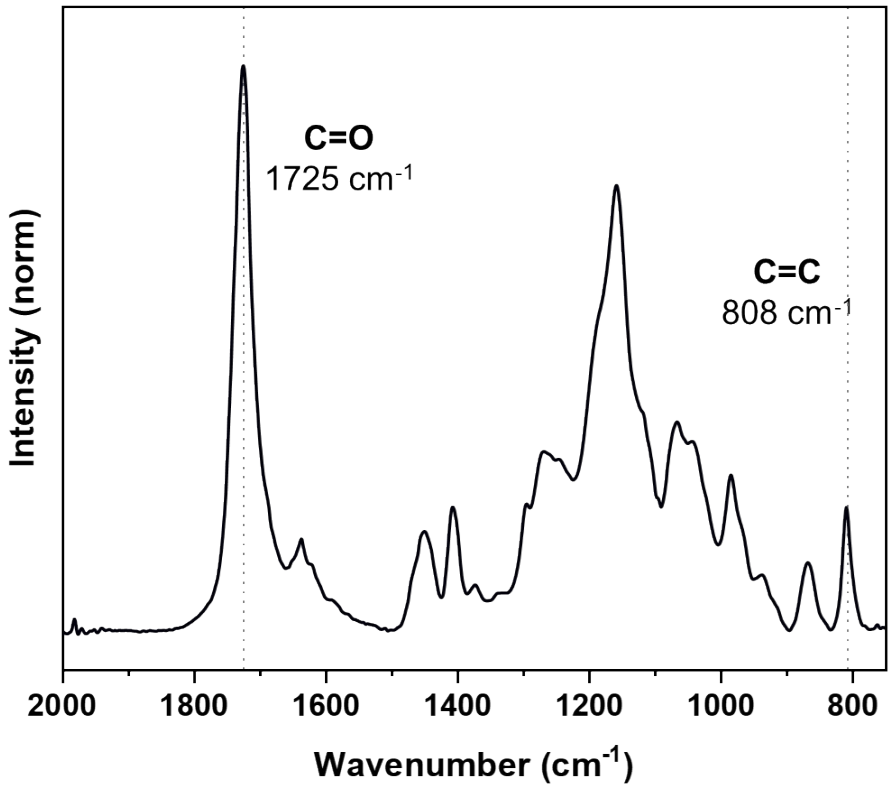

Figure S3: Representative FT-IR spectrum of 3D microprinted BA-co-Acryl structure. Signals at 808 and 1725 cm^{-1} correspond to v(C=C) (acrylate), and v(O-C=O) (ester), respectively. Integration values of the peaks were used for further calculations.

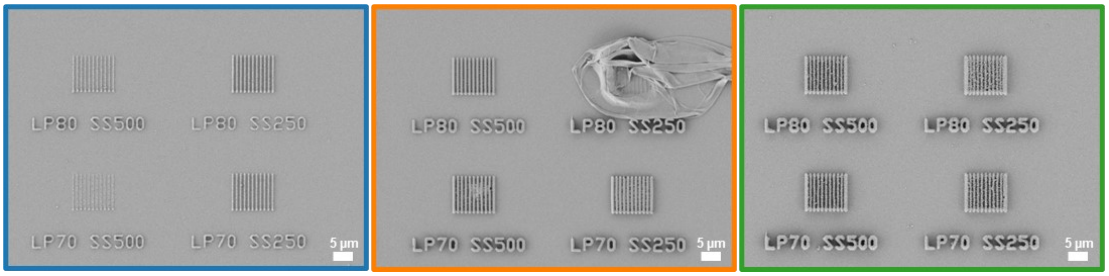

Figure S4: Single line printing patterns printed using BA-co-Acryl (left, blue), MA-co-Acryl (middle, orange) and IBA-co-Acryl (right, green).

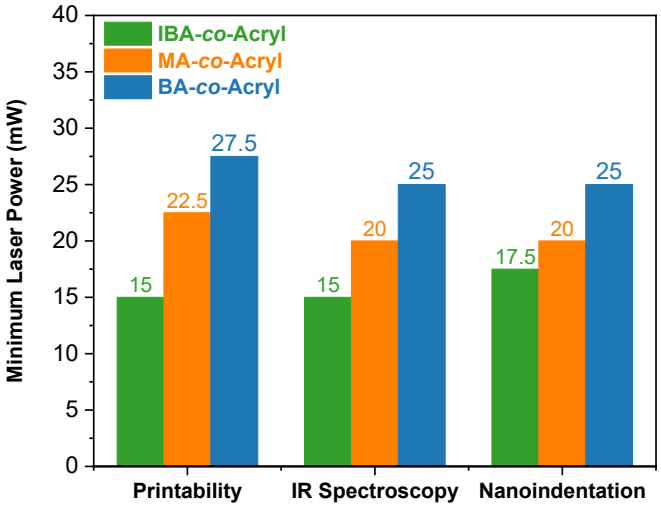

Figure S5: Lowest minimum laser power required to achieve measurable 2PLP structures used for characterization of printability, IR spectroscopy and nanoindentation.