Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Designing Adaptive Materials for 3D-Printing via Dynamic Covalent Imine Bonds

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1 Materials and methods

All commercially available solvents and Monomers were used without further purification. We used 2-[[(Butylamino)carbonyl]oxy] ethyl acrylate (2BAEA), Diphenyl (2,4,6-trimethyl-benzoyl) phosphine oxide (PI) and Poly(ethyleneglycol)-dimethacrylate (PEGDMA) (M_n = 750 g/mol) 2,4-Dihydroxybenzaldehyd, Triethylamine and Methacrylic anhydride from Sigma-Aldrich. The chemicals for synthesis for amine component like 4-aminothiophenol and 3-chloro-2-hydroxypropyl methacrylate was purchased from Merck. Solvents we used in analytical grade were Methanol, THF, DMF. For washing the samples we used isopropanol in technical standard.

^{1}H-, and ^{13}C-NMR-spectroscopy were measured at room temperature in deuterated solvents using a Bruker AV Neo 400. The mass spectra were measured by electron spray ionisation using the maXis 4G from Bruker.

FTIR-spectra and characterization of the chemical structure and curing behaviour were recorded on a Jasco FT/IR 4600 equipped with an ATR-crystal. FTIR spectra of the 3D-printed resins were recorded both before and after the printing process. For the curing measurements, a small drop of uncured resin was placed directly onto the ATR crystal and analysed. The sample was then exposed to UV light (intensity: 4,288 mW/cm^2, peak wavelength: 402 nm) from 7 cm above the surface for varying irradiation times. The number of scans were set to 35 and performed in the range of 4000 to 400 cm^{-1} with a resolution of 4 measurements were recorded in absorbance. Fluorescence spectra were recorded on an RF-6000 from Shimadzu Corporation with scan speed of 600 nm/min and Excitation and Emission Bandwidth of 5.0 nm.

The surface topography was examined by scanning electron microscopy (SEM) using an Apreo S LoVac instrument (Thermo Fisher Scientific, USA). Prior to analysis, the samples were coated with a conductive platinum layer via magnetron sputtering. The elemental composition was analyzed by energy-dispersive X-ray spectroscopy (EDX) with an UltraDry EDS detector (Thermo Fisher Scientific, USA).

Viscosity was done on a TA instruments Discovery HR 20. The diameter of the plates was 25 mm and the distance between the two geometries was 300 µm. Flow sweep measurements were performed at 23 °C with a shear rate from 1 to 100 s^{-1}.

3D printing was carried out using an Anycubic, Photon Mono 2 (DLP) 3D printer equipped with a 405 nm upgraded LighTurbo Matrix light source, providing an irradiance of 4.2 mW/cm^2. 3D models were designed using Autodesk Inventor Professional Version 2024.2 and all samples were printed with a layer height of 100 µm, exposure time of 11 s for resin **P0, P3** and 80 s for resins **P1** and **P2** to ensure full curing. The bottom exposure time of resin **P0, P3** was set to 12 s and for resins **P1** and **P2** bottom exposure time of 80s and 0.5 s off time. The bottom layers were set to 6 and anti-alias was 16. After printing, samples were washed in isopropanol (IPA) for 5 minutes, air-dried for 10 minutes and post-cured for 4 minutes at room temperature using a wash and cure station from Anycubic. Before printing, a working curve was created for each formulation to determine the required exposure time for achieving the 100 µm layer thickness. To prepare the working curve resin was filled at the bottom of a clean and empty resin tank. The formulation was applied using a pipette to fully cover the tank. Each 5x5 mm^2 plate was exposed to varying irradiation times (from 9 to 200 seconds) without the use of a build platform. Carefully the exposed plates were taken and then thoroughly cleaned using a fresh cloth. Any unreacted resin was carefully rinsed off with isopropyl alcohol (IPA). The cured layer thickness was measured using the gap function of the Rheometer of TA instruments Discovery HR 20 to establish the working curve, showing the relationship between exposure time and layer thickness. Each measurement was done tree times.

Contact angle measurements were recorded using a Dataphyics OCA-11. Each plate was coated with an aldehyde or amine derivative, and the contact angle was measured five times.

Tensile tests were performed on a Shimadzu AGS-X with a 10 kN load cell and a speed of 25 mm/min at room temperature. All samples were tested a room temperature of 23°C ± 2°C. A minimum of three specimens per resin formulation were measured. The stress is given in MPa and the elongation is given in %. Test speed was set to 25 mm/min. For the mechanical properties of the 3D-printed parts, tensile bars with a length of 75 mm, a width of 5 mm, and a thickness of 2 mm were printed. For the welding experiments we used a modified form. Here the sample dimensions were 5x1x12 mm, but the positive samples had an arrowhead on the top with an angle of 45° and a length of 5 mm. The negative moulded parts had a wedge-shaped indentation and an angle of 45° and a depth of 5 mm.

2 Identification and characterization of the host resin

The photopolymer resin R71.6 referred as P0 in this publication was developed through systematic optimization of multiple resin formulations. The initial formulation, designated P49, comprised a highly brittle photopolymer consisting of 60 wt.% tetrafunctional acrylate crosslinker, 1 wt.% photoinitiator Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), 9 wt.% acrylate diluent 2 [[(butylamino)carbonyl]oxy]ethyl acrylate (2BAEA), and 30 wt.% methacrylate monomer. This material did not exhibit sufficient welding capability to join materials effectively. We must need a more flexible polymer.

To improve both viscosity (see Figure S10) and flexibility, an intermediate formulation (**P61**) was developed by reducing the tetrafunctional acrylate crosslinker content to 20 wt.% and introducing a diacrylate linker at 70 wt.%. This composition exhibited significantly enhanced elongation and improved viscosity. However, stress cracking within the polymer matrix was observed over time.

To address this issue, the diacrylate linker concentration was increased to 90 wt.% while the tetrafunctional crosslinker was completely removed (**P63**). This resulted in a resin with very favourable viscosity and flexibility. Initially attempts to utilize this resin in 3D printing have proven challenging, primarily due to insufficient mechanical stability required for consistent and reliable printing performance.

In a final optimization step, the formulation was refined by replacing the diacrylate linker with 30 wt.% of a polyethylene glycol-based linker (PEGDMA). The formulation was further adjusted to contain 1 wt.% photoinitiator (PI) and 69 wt.% of 2-[[(butylamino)carbonyl]oxy]ethyl acrylate (2BAEA). This final composition demonstrated both good printability and desirable viscosity characteristics (see Figure S6). Table 1 provides an overview of the resin formulations developed during this optimization process, including the final composition P71.6 (**P0**) used in this work.

Table S1: Composition of the optimized photopolymers P71 and P71.6.

Name Photopolymer	TPO wt.%	2BAEA wt.%	PEGDMA wt.%	comment
P71.0	1	69	30	Flexible but sticky
P71.2	1	59	40	semi Flexible
P71.3	1	49	50	Unflexible, brittle
P71.4	1	89	10	Sticky
P71.5	1	99		Very flexible and very sticky
P71.6 (P0)	1	94	5	Best performance of flexibility, toughness and welding properties

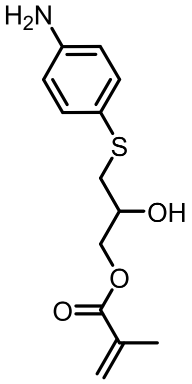
In DLP 3D printing process it is necessary to have a lower viscosity than 2000 mPa*s to allow good recoating of the resin during printing process. [1, 3]The viscosity of the photopolymer formulations was evaluated. The host polymer **P0** exhibited a viscosity of 0.029 Pa·s.

3 Synthesis of imines on the 3D printed surface and exchange reactions

The formation of imine functionalities on the 3D-printed object was achieved by immersing the samples **P1** and **P2** into a 0.01 molar aldehyde solution for 5 minutes. Subsequently, the object was removed from the solution washed with pure Methanol and allowed to air dry under ambient conditions for 15 minutes. The exchange reaction was carried out using the same settings, but the sample was immersed in a 0.01M aldehyde solution for 2 hours and after each 15 minutes the aldehyde solution was replaced with fresh produced 0.01M aldehyde solution in methanol.

4 Synthesis of Amine and Aldehyde monomers

4.1 Synthesis of Am-M1

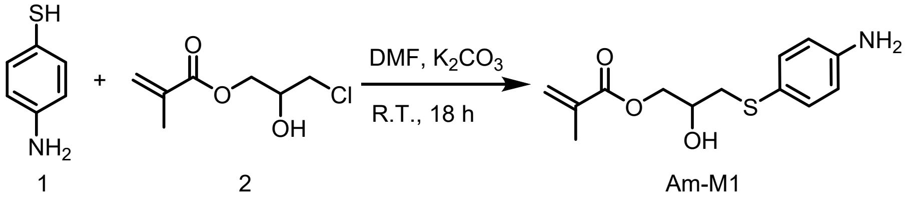


Am-M1 was synthesised as follows. 1.158 g of molten 4-aminothiophenol (3) was dissolved in a 100 mL round bottom flask dissolved in 20 mL DMF, cooled to 0 °C in an ice bath and diluted by adding 1.538 mL TEA and then 1.67 mL of 3-chloro-2-hydroxypropyl methacrylate (4) were added. After 20 minutes, the ice bath was removed, and the reaction mixture was stirred at stirred overnight at room temperature. The reaction solution was then poured onto 150 mL of water and extracted four times with 20 mL of ethyl acetate. The combined organic phases were diluted with 150 mL saturated sodium hydrogen carbonate solution and washed twice with 200 mL saturated sodium chloride solution, dried over dried over sodium sulfate, and the solvent was removed under reduced pressure. The purification was carried out by column chromatography over silica gel with CH:EA in a ratio 3:2. Yield: 1.037 g (81%)

^{1}H-NMR (400 MHz, DMSO-d6), δ [ppm]: 7.10 (d, J = 6.5, 2H), 6.52 (d, J = 1.9, 2H), 5.50 (dd, J = 5.4, 1.6, 2H), 5.27 (s, 1H), 4.06 - 3.94 (m, 2H), 3.92 - 3.84 (m, 1H), 3.64 (d, J = 12.0, 1H), 3.60 - 3.53 (m, 1H), 2.99 - 2.90 (m, 1H), 2.78 - 2.70 (m, 1H), 1.14 (dd, J = 10.8, 7.0, 3H).

^{13}C{1H}-NMR (101 MHz, DMSO-d6), δ [ppm]: 174.62, 149.24, 134.69, 134.64, 118.38, 114.87, 68.41, 65.51, 65.46, 60.22, 46.96, 46.92, 16.75.

FT-IR *ν* (ATR) [cm^{-1}]: 3374, 2975, 1718, 1618, 1595, 1494, 1273, 1156, 1117, 817



Scheme S1: General procedure of the synthesis of compound **Am-M1**.

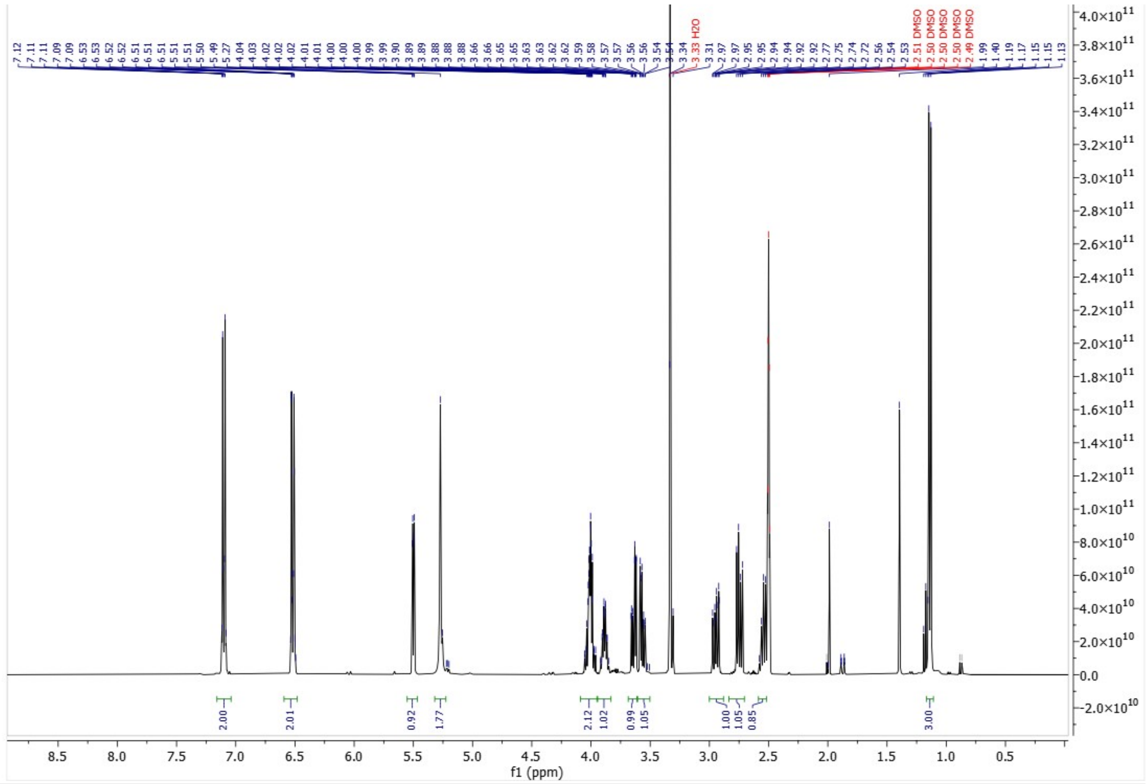


Figure S2: ^{1}H-NMR spectrum of **Am-M1** in DMSO-d6.

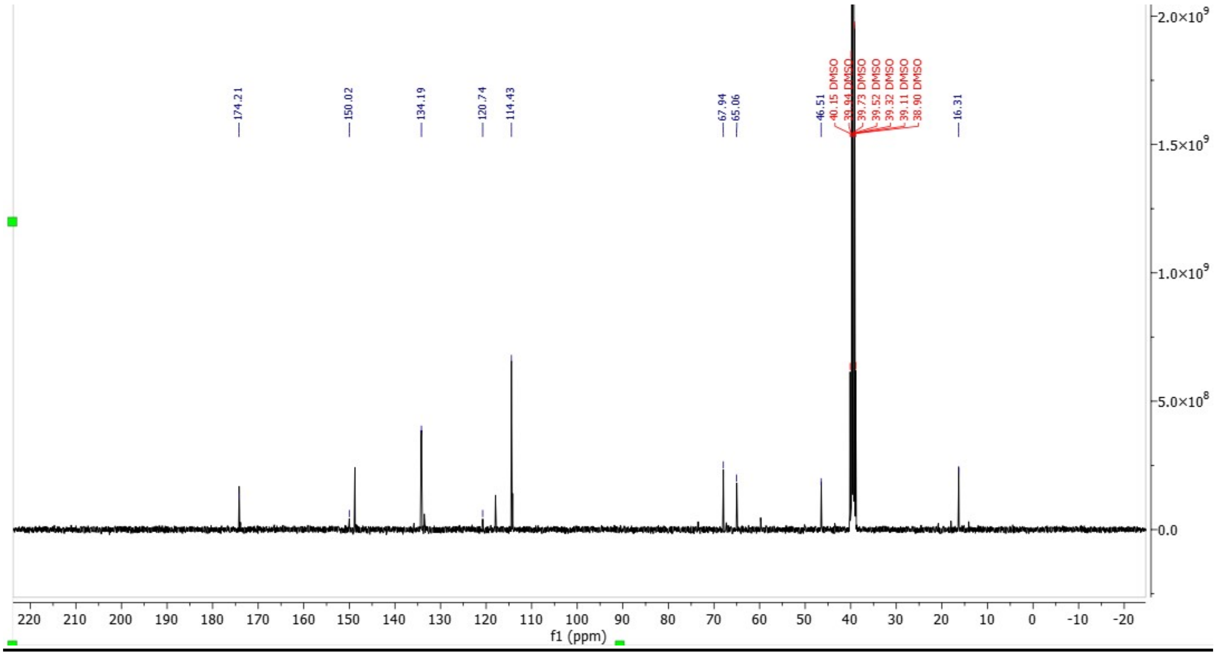
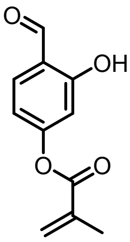


Figure S3: ^{13}C{1H}-NMR spectrum of **Am-M1** in DMSO-d6.

4.2 Synthesis of Ald-M3



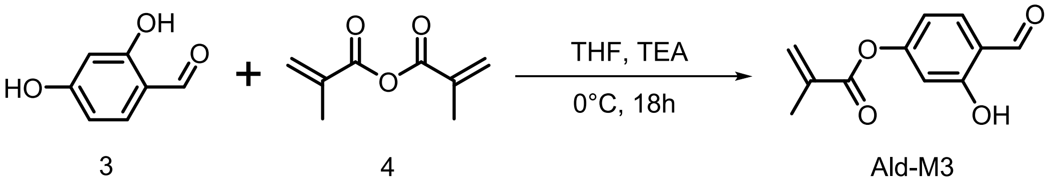
Ald-M3 was synthesised as follows. In a 250 mL round bottom flask, 2,4-dihydroxy-benzaldehyde (3.77 g, 0.027 mol, 1 eq.) were dissolved in 50 mL THF and triethylamine (7.04 mL, 0.038 mol, 1.4 eq.) were added and cooled to 0 °C with an ice bath. After that methacrylic anhydride (5.69 mL, 0.038 mol, 1.4 eq.) were added slowly dropwise and the reaction mixture was stirred at room temperature for 18 hours. After the reaction is completed (check via DC), 10 mL of water was added and stirred for further 30 minutes before it was transferred to 150 mL of water to a separating funnel. The mixture was extracted three times with 100 mL ethyl acetate, the combined organic phases were washed with 250 mL saturated sodium chloride solution, dried over sodium sulphate, filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (cyclohexane : ethyl acetate 19:1). Alternatively, the compound could be purified by sublimation at 100 °C and 0.3 mbar. Yield: 2.30g, 59%.

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 11.22 (s, 1H), 9.86 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 6.82 (dd, J = 10.9, 8.8 Hz, 1H), 6.78 (d, J = 2.1 Hz, 1H), 6.36 (p, J = 1.0 Hz, 1H), 5.80 (p, J = 1.5 Hz, 1H) 2.06 - 2.04 (m, 3H)

^{13}C{1H}-NMR (101 MHz, $CDCl_3$) δ = 195.60, 164.88, 163.26, 157.77, 135.05, 128.34, 118.73, 114.07, 110.84, 27.02, 18.40

FT-IR ν (ATR) [cm^{-1}]: 3192, 2979, 1727, 1654, 1577, 1494, 1278, 1152, 1126, 1114

HR-MS (ESI pos., MeOH, C11H10O4 + H+) [m/z] calculated: 207,20, found: 207,65



Scheme S4: General procedure of the synthesis of compound **Ald-M3**.

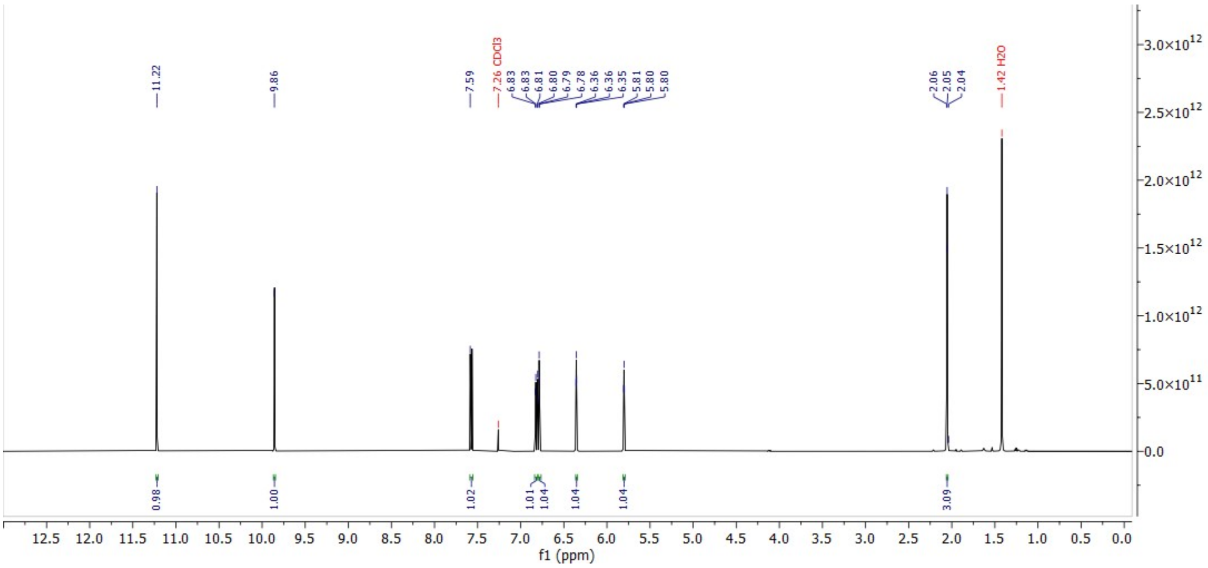


Figure S5: ^{1}H-NMR spectrum of **Ald-M3** in CDCl$_3$.

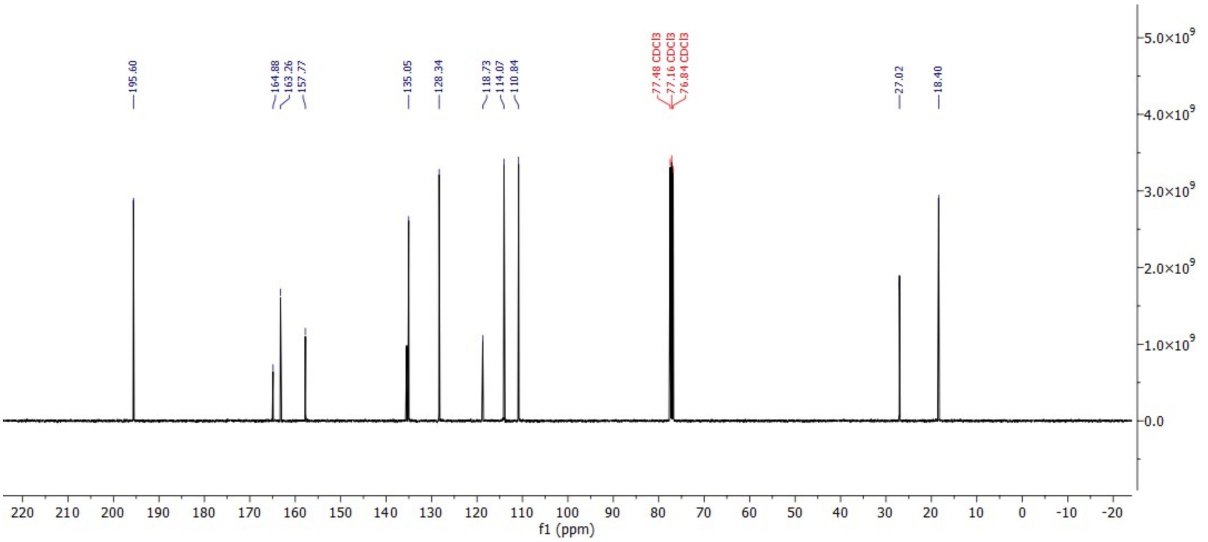


Figure S6: ^{13}C{1H}-NMR spectrum of **Ald-M3** in CDCl$_3$.

5 Determination of curing parameters

For the 3D printing process, a layer thickness of 100 µm was selected as the preferred height. Printing parameters were determined using working curves performed in triplicate. The resulting layer thickness (µm) is plotted as a function of exposure time (s) in the working curves shown in Figures S7.

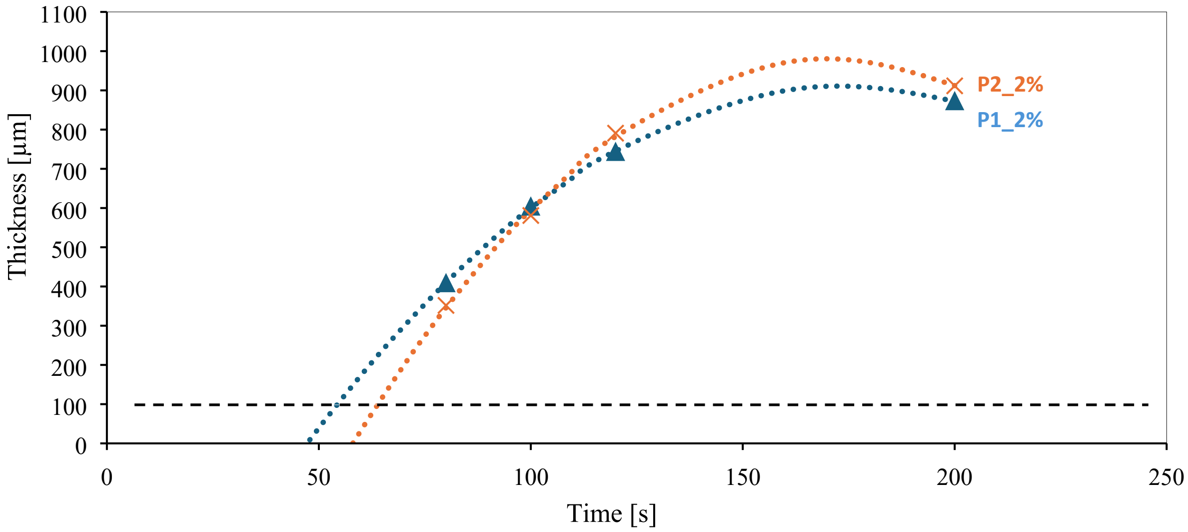


Figure S7: Working curves for Resin P1 (blue, triangle), P2 (orange, cube) are shown. The intersection points of the trend lines with the horizontal line at y = 100 µm are used to determine the minimum exposure time required for theoretical successful 3D printing. For real 3D printing tests the exposure time was set to 80s.

6 Rheological data

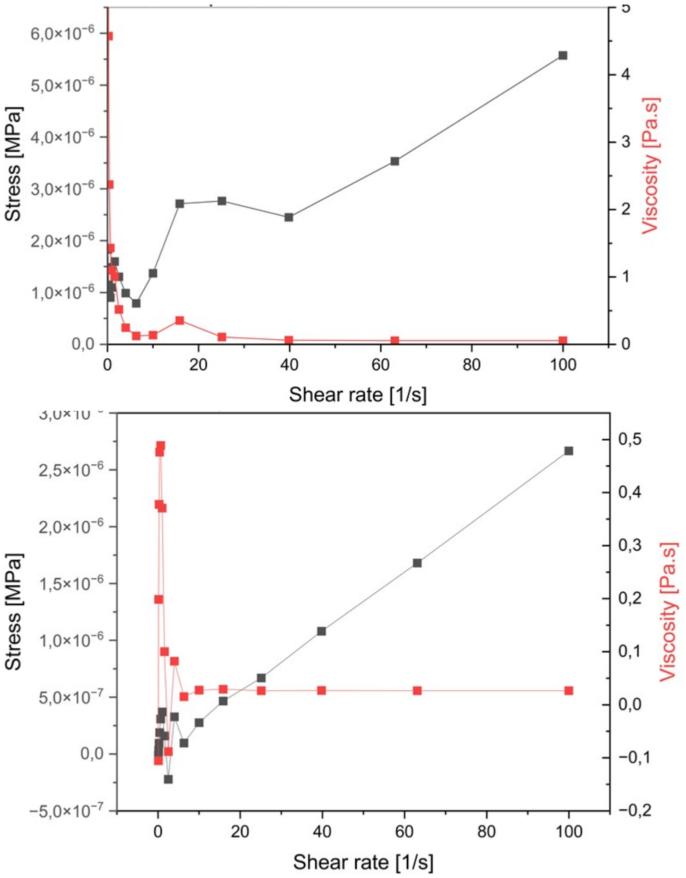


Figure S8: Measurement of the viscosity of photopolymers P1 above and P2 bottom.

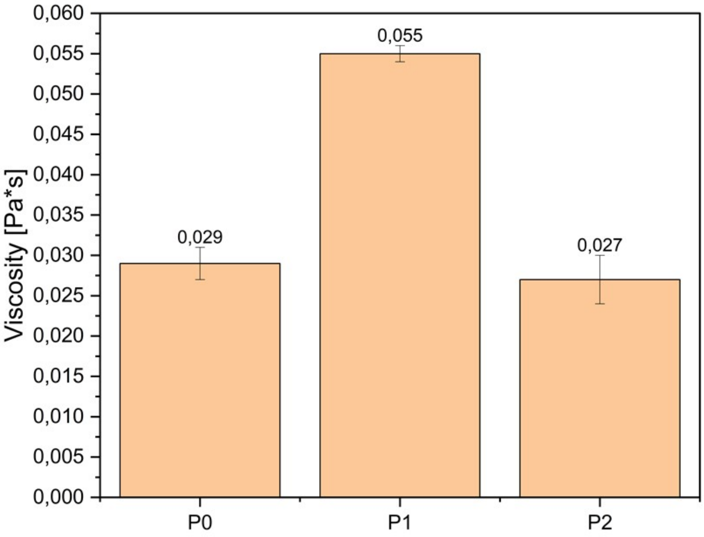


Figure S9: Measurement of the viscosity of photopolymers P0, P1 and P2.

7 FT-IR Data

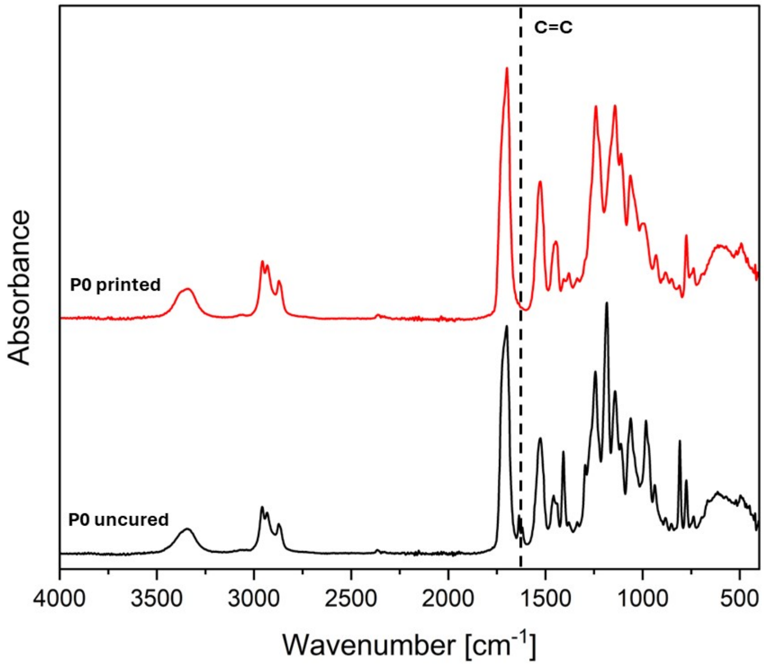


Figure S10: FT-IR spectra of resin P0, uncured (black) and printed (red). Dotted line marks the C=C conversion.

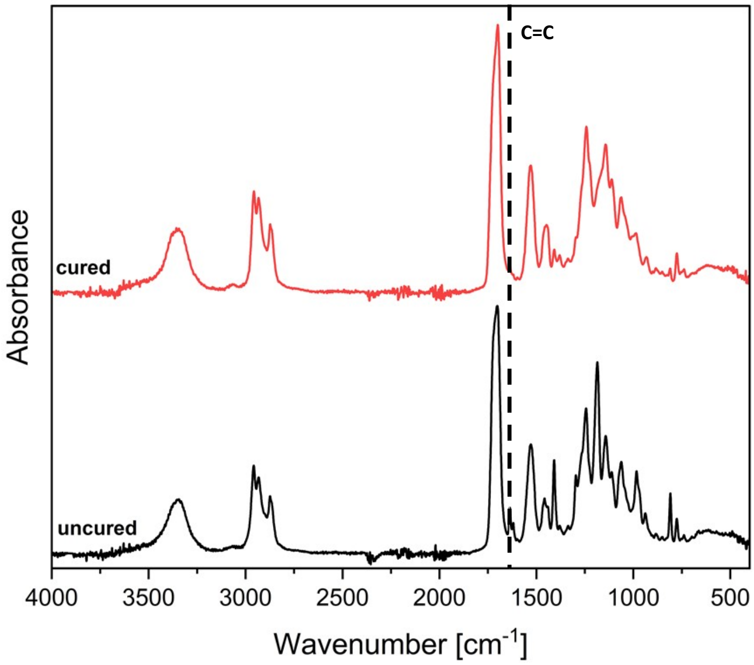


Figure S11: FT-IR spectra of resin P1, uncured (red) and printed (black). Dotted line marks the C=C conversion.

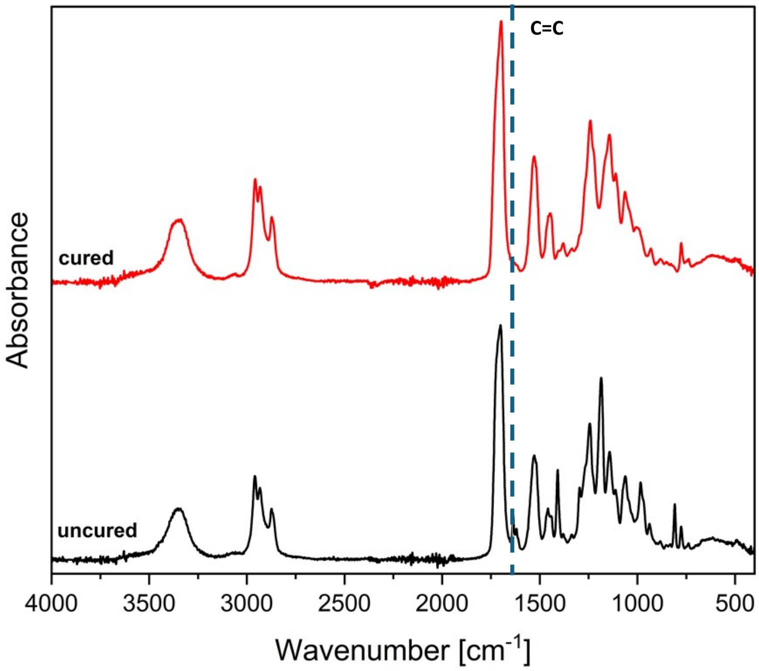


Figure S12: FT-IR spectra of resin P2, uncured (black) and printed (red). Dotted line marks the C=C conversion.

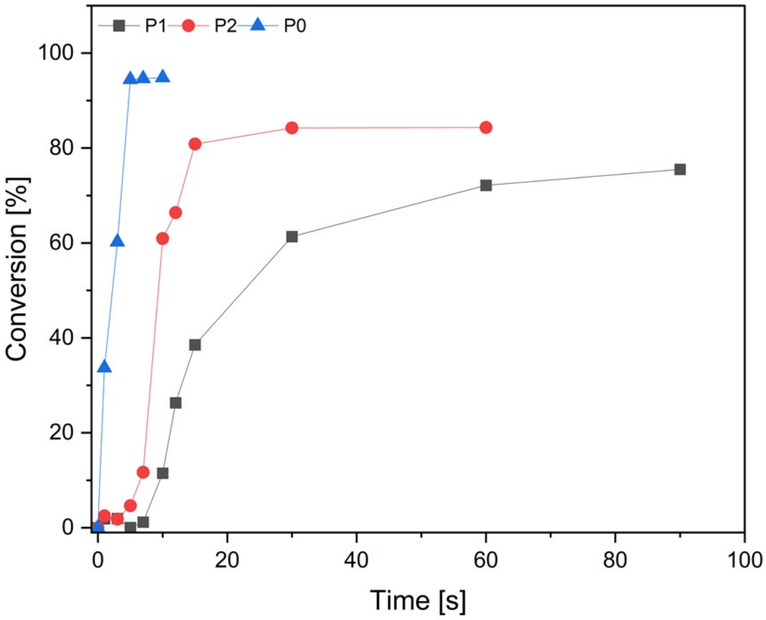


Figure S13: Conversion of the C=C double bonds of polymer P0, P1 and P2.

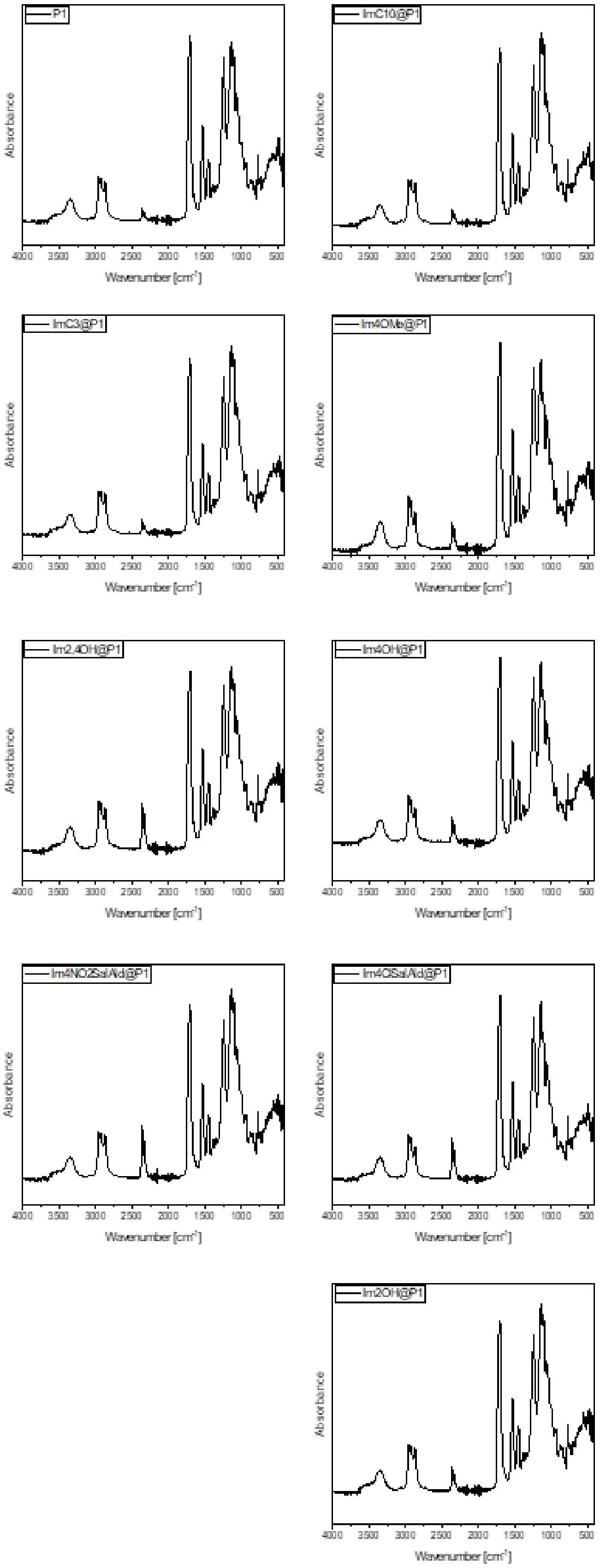


Figure S14: Comparison of FT-IR spectra of P1 coated with different aldehydes on polymer surface.

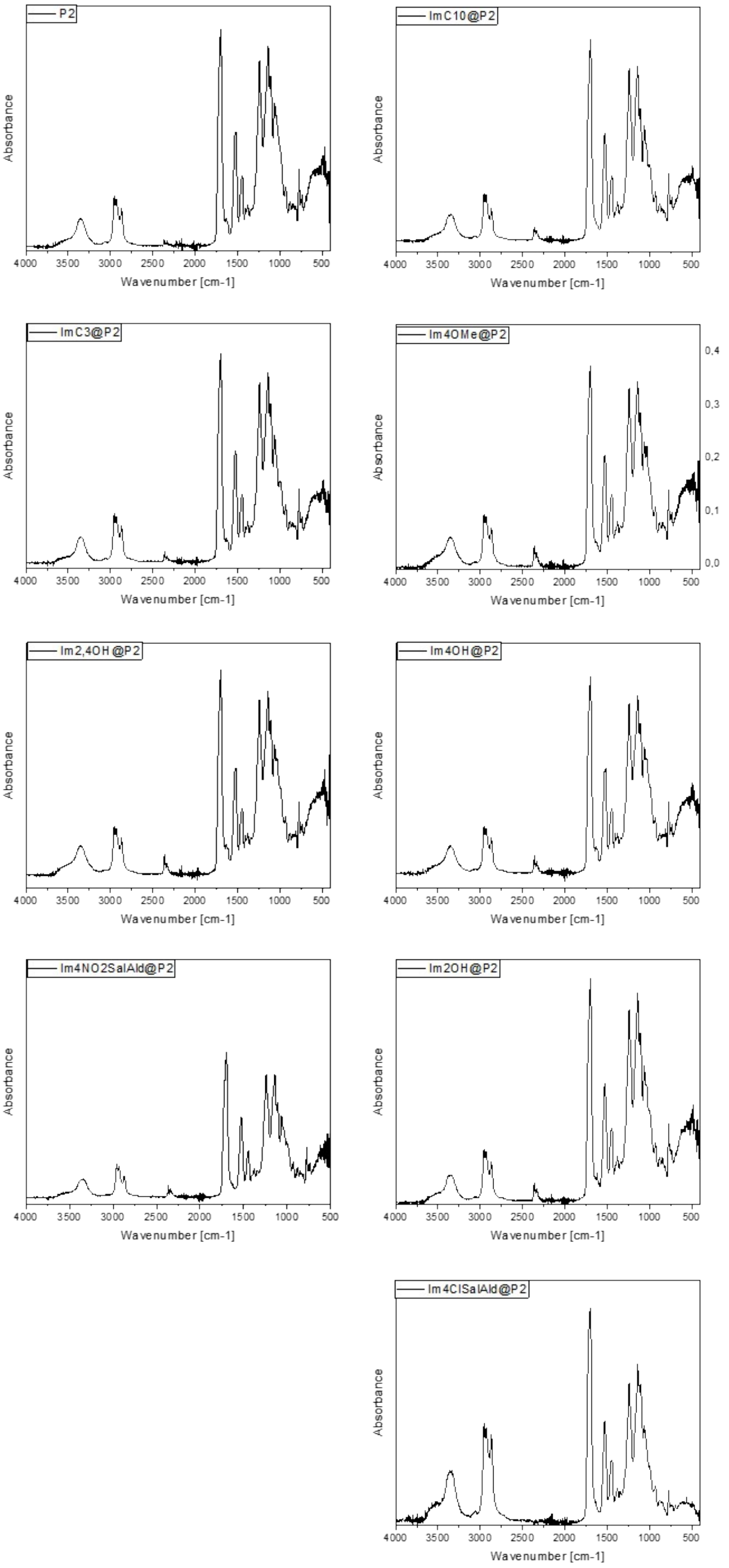


Figure S15: Comparison of FT-IR spectra of P2 coated with different aldehydes on polymer surface.

8 Contact angle measurements

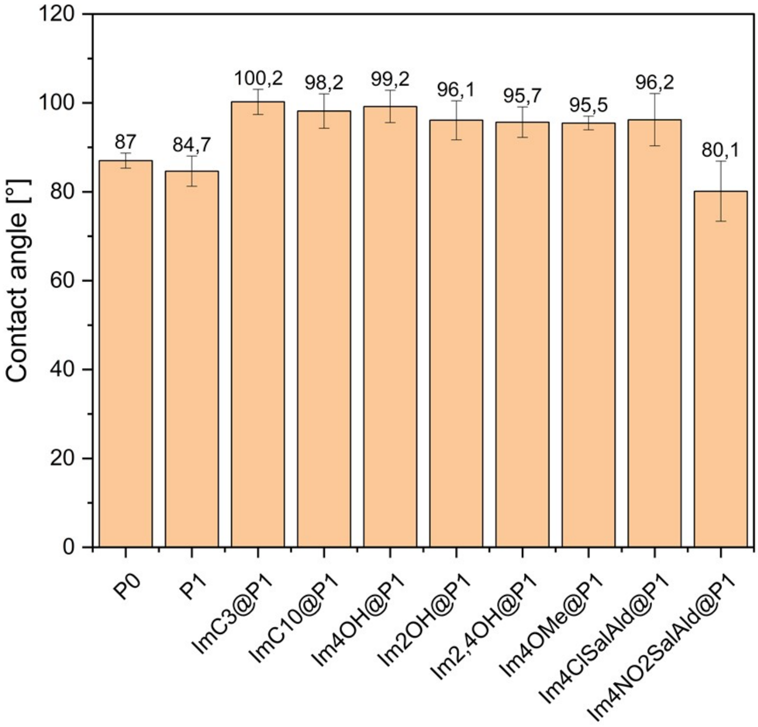


Figure S16: Contact angles of the imines to water of P1. P 1 coated with C3 = propionaldehyde C10 = decan aldehyde, 4OH = 4-hydroxybenzaldehyde, 4OMe = 4methoxybenzaldehyde, 2,4OH = 2,4dihydroxybenzaldehyde, 2OH = 2 hydroxybenzaldehyde, 4Cl2OH = 4 chloro-2 hydroxybenzaldehyde, 4NO2 2OH = 4 nitro 2 hydroxybenzaldehyde.

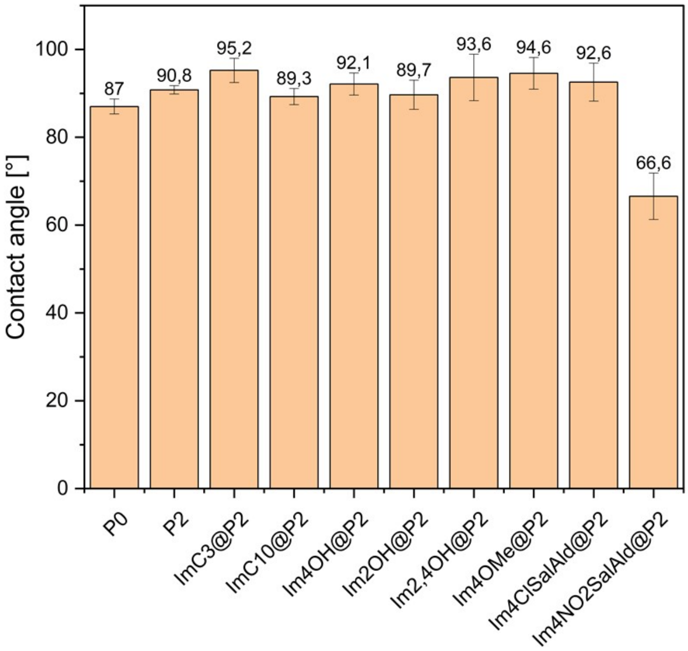
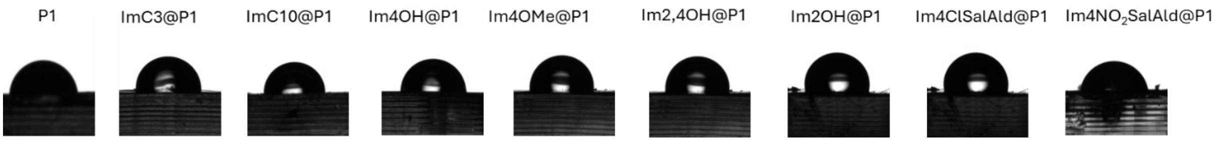
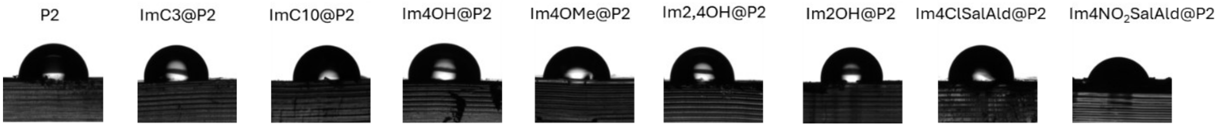


Figure S17: contact angles of the imines to water of P2. P2 coated with C3 = propionaldehyde C10 = decan aldehyde, 4OH = 4-hydroxybenzaldehyde, 4Me = 4-methylbenzaldehyde, 4OMe = 4methoxybenzaldehyde, 2,4OH = 2,4dihydroxybenzaldehyde, 2OH = 2 hydroxybenzaldehyde, 4Cl2OH = 4 chloro-2 hydroxybenzaldehyde, 4NO2 2OH = 4 nitro 2 hydroxybenzaldehyde.



Fotos: S18: Static contact angle images of water at the photopolymer surface of P1 coated with C3 = propionaldehyde C10 = decanaldehyde, 4OH = 4-hydroxybenzaldehyde, 4OMe = 4methoxybenzaldehyde, 2,4OH = 2,4dihydroxybenzaldehyde, 2OH = 2 hydroxybenzaldehyde, 4Cl2OH = 4 chloro-2 hydroxybenzaldehyde, 4NO_2 2OH = 4 nitro 2 hydroxybenzaldehyde.



Fotos: S19: Static contact angle images of water at the photopolymer surface of P2 coated with C3 = propionaldehyde C10 = decan aldehyde, 4OH = 4-hydroxybenzaldehyde, 4OMe = 4methoxybenzaldehyde, 2,4OH = 2,4dihydroxybenzaldehyde, 2OH = 2 hydroxybenzaldehyde, 4Cl2OH = 4 chloro-2 hydroxybenzaldehyde, 4NO_2 2OH = 4 nitro 2 hydroxybenzaldehyde.

9 Emission measurements

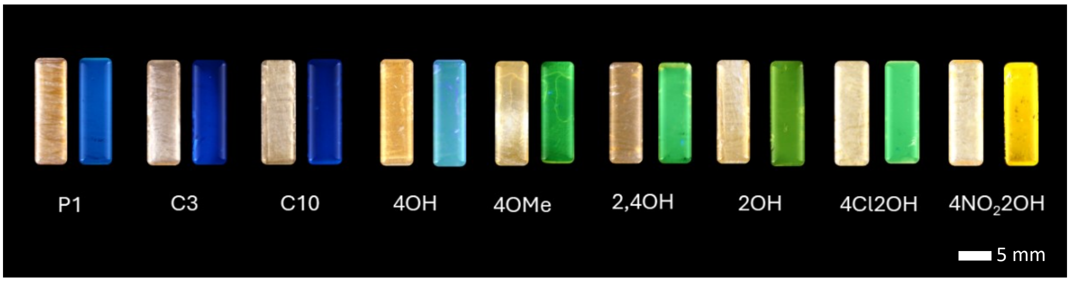


Figure S20: a) Emission wavelength of P1 coated with different aldehydes. Excitation 365nm. B) Photos of coated Photopolymer P1 with different aldehydes. P1 =base polymer with **Am-M1**, C3 = Propionaldehyde, C10 = Decanaldeyhde, 4OH = 4 Hydroxybenzaldehyde, 4Ome = 4 Methoxybenzaldehyde, 2,4OH = 2,4 Dihydroxybenzaldehyde, 2OH = Salicylaldeyhde, 4Cl2OH = 4 Chloro-2hydroxybenzaldehyde, 4NO$_2$2OH = 4 Nitro-2hydroxybenzaldehyde. Left under daylight, right under UV-light (365nm).

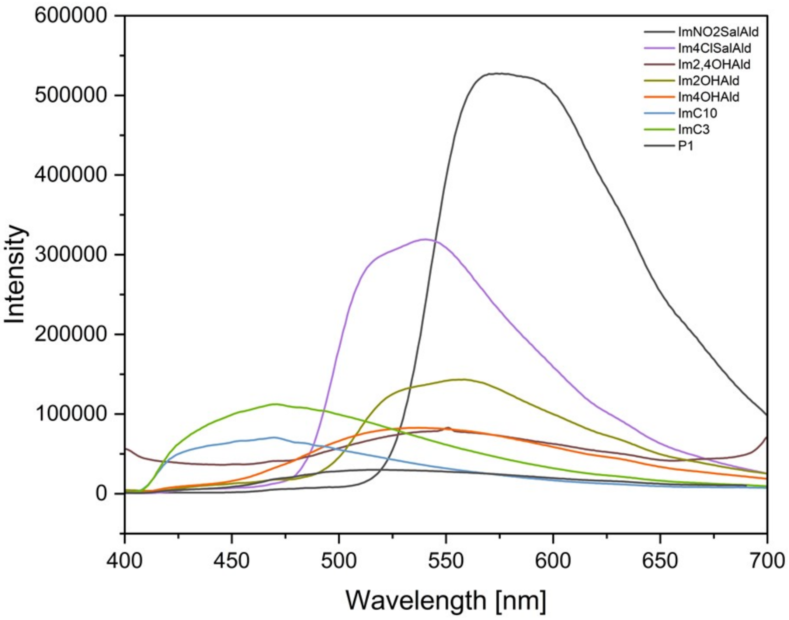


Figure S21: Emission wavelength of P1 with absolute intensities. Excitation 365nm.

Table S2: Peak maxima of Am-M1 and P1 coated with different aldehydes. Excitation wavelength at 365nm.

	Am-M1	P1	Im C3	Im C10	Im 4OH	Im 4OMe	Im 2,4OH	Im 2OH	Im 4Cl2OH	Im 4NO$_2$2OH
λ_{Em} [nm]	501	517	471	470	533	549	548	555	540	576

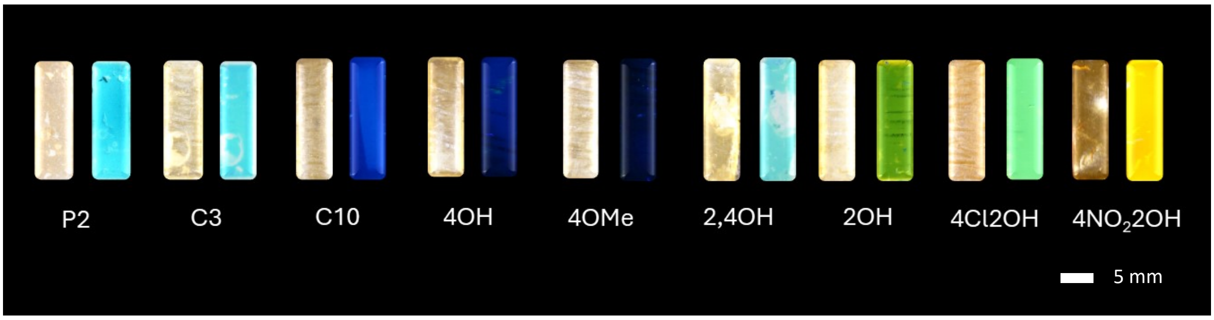


Figure S22: A) Emission wavelength and shifts of P2 coated with different aldehydes. Excitation 365nm. B) Photos of coated Photopolymer P2 with different aldehydes. P2 =base polymer with Am-M2, C3 = Propionaldehyde, C10 = Decanaldeyhde, 4OH = 4 Hydroxybenzaldehyde, 4Ome = 4 Methoxybenzaldehyde, 2,4OH = 2,4 Dihydroxybenzaldehyde, 2OH = Salicylaldeyhde, 4Cl2OH = 4 Chloro-2hydroxybenzaldehyde, $4NO_22OH$ = 4 Nitro-2hydroxybenzaldehyde. Left under daylight, right under UV-light (365nm).

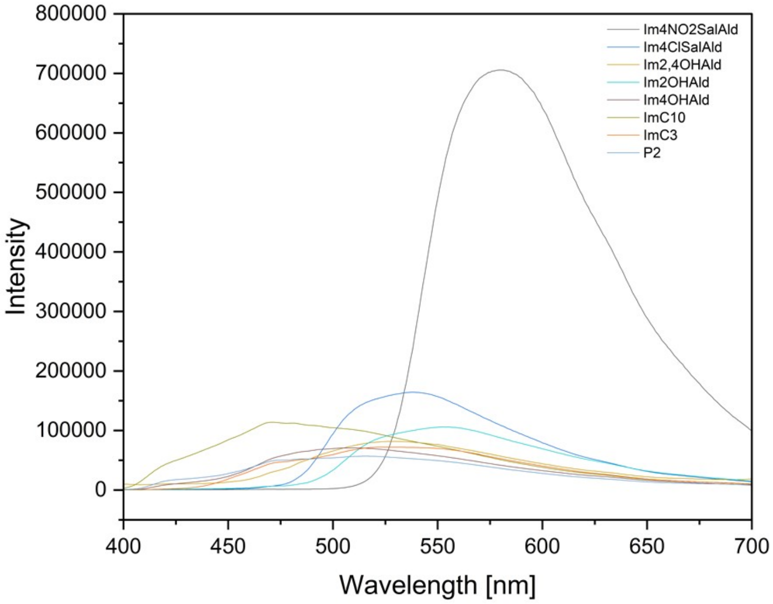


Figure S23: Emission wavelength of P2 with absolute intensities. Excitation 365nm.

Table S3: Peak maxima of Am-M2 and P2 coated with different aldehydes. Excitation wavelength at 365nm.

	Am-M2	P2	Im C3	Im C10	Im 4OH	Im 4OMe	Im 2,4OH	Im 2OH	Im 4Cl2OH	Im $4NO_22OH$
λ_{Em} [nm]	372	518	523	471	509	495	529	555	538	581

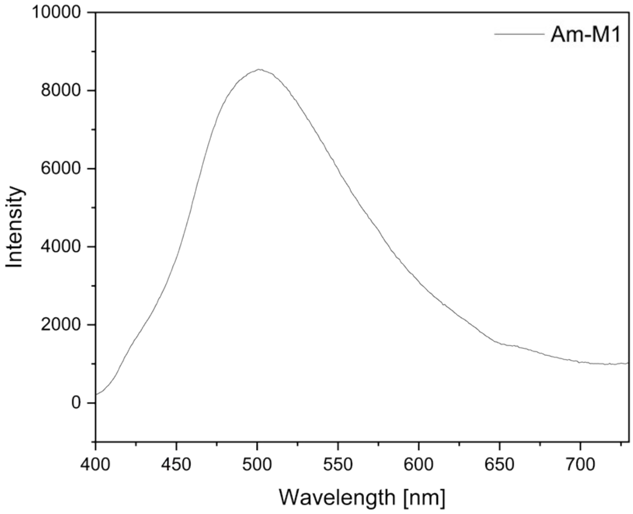


Figure S24: Fluorescence emission of Monomer Am-M1. Excitation of 380 nm emission peak 501 nm.

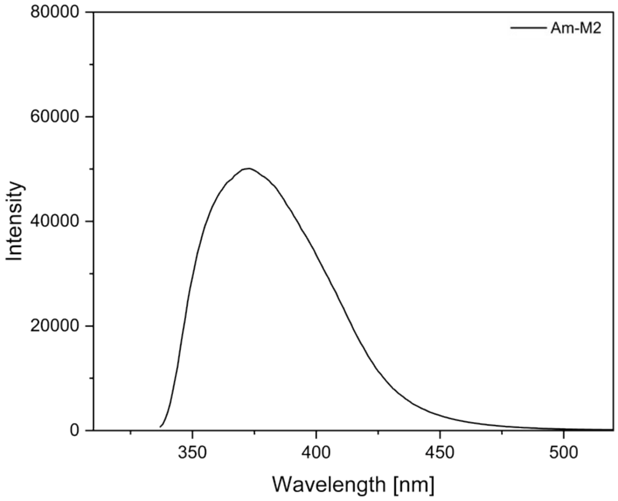


Figure S25: Fluorescence emission of monomer Am-M2. Excitation of 322 nm and emission peak at 372 nm.

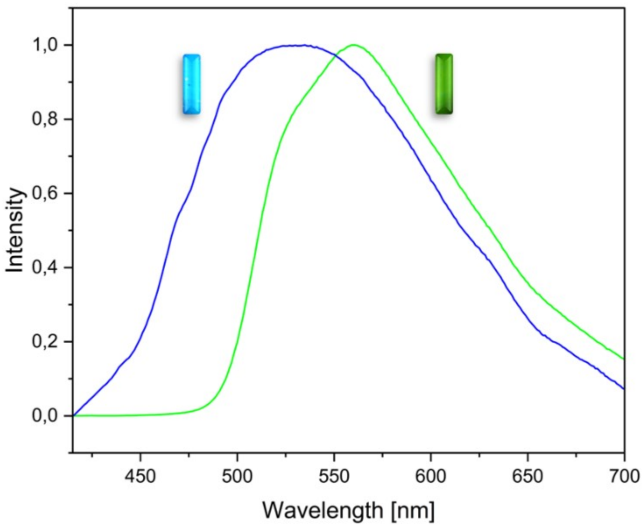


Figure S26: Exchange reaction of P1 from 4 hydroxybenzaldehyde (blue curve) with 2 hydroxybenzaldehyde (green curve). Excitation with 395 nm.

10 Tensile Test

Preliminary studies have shown that two main factors must be optimized to achieve particularly strong adhesion. First, the polymer must possess sufficient softness. In this context, a Shore hardness of approximately 60–70 has proven to be particularly favourable (see table S4). Second, to achieve adequate interfacial bonding between the two surfaces, the temperature must increase to 80 °C to ensured good flexibility and interface connection.

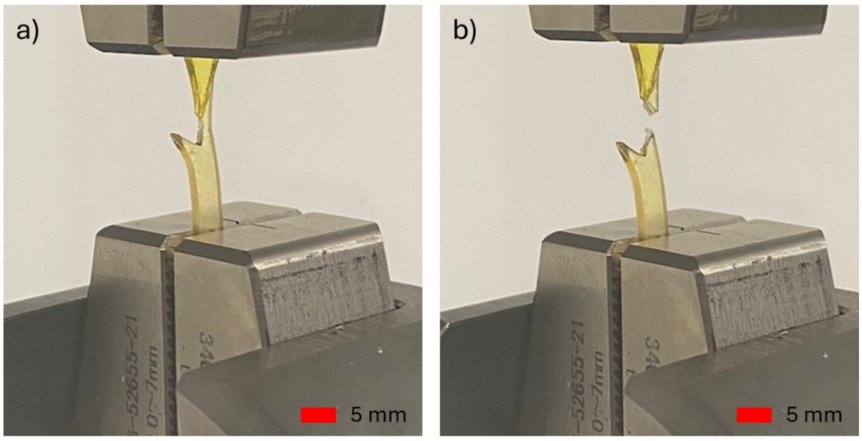


Figure S27: General setup of the tensile test. 3D-printed specimens with modified sample geometry. Polymer **P1** (top) and **P3x10** (bottom) were tested after conditioning at 80 °C for 24 hours in an oven. Images show the samples during testing with asymmetric rupture (a), and after testing (b).

Table S4: Measurements of the SHORE Hardness of polymer P0, P1, P2 and P3.

Polymer	**P0**	**P1**	**P2**	**P3**
Shore Hardness A	60	63	65	71

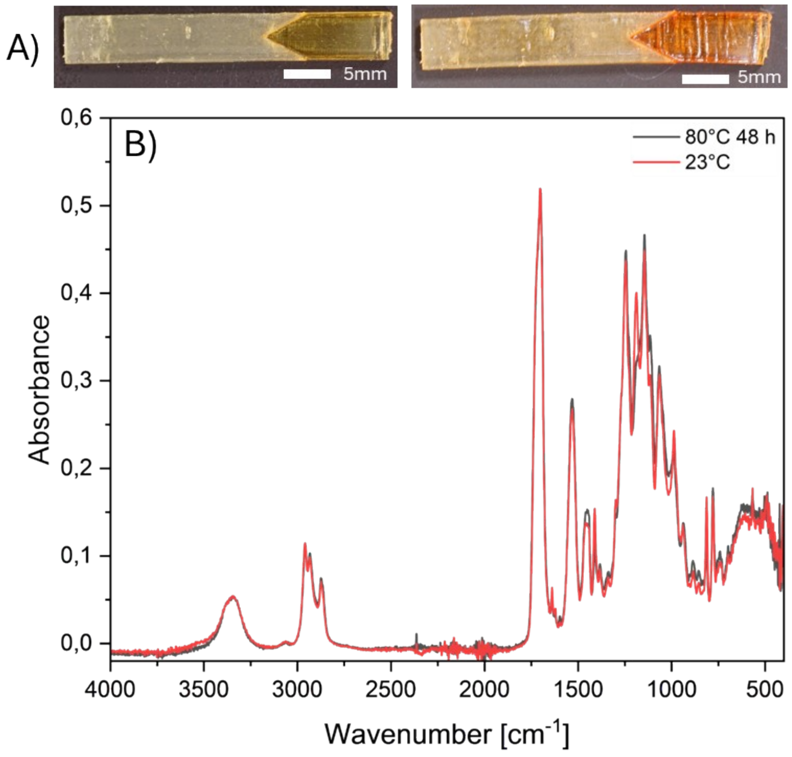


Figure S28: Photos of little cracks and color change at the polymer surface of sample P2 for 2 days in oven at 80°C. Left before and right after heat treatment.

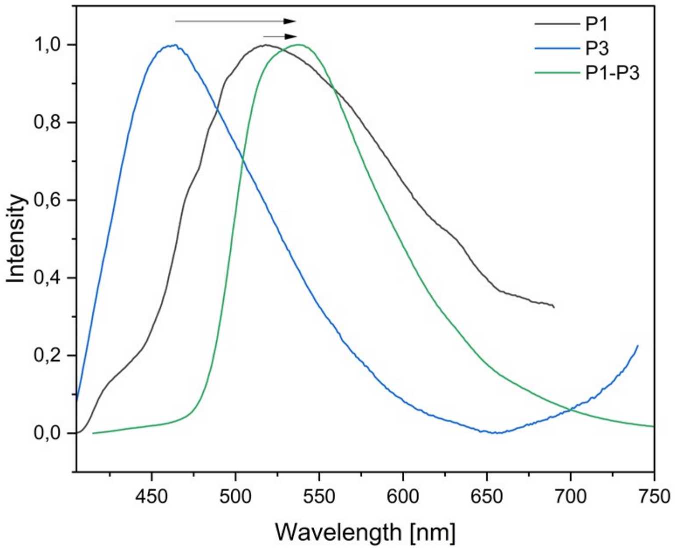


Figure S29: Emissions shift of the polymer sample P1 and P3 upon interface reaction to form imine bonds and give new signal from P1-P3 at 537 nm.

11 SEM Measurements

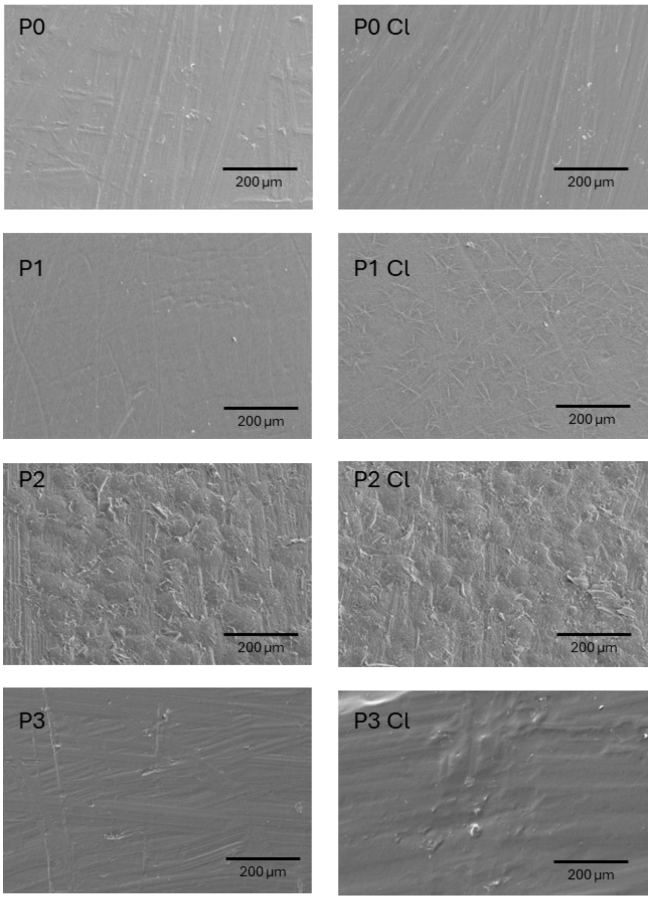


Figure S30: SEM measurements of samples P0, P1, P1 Cl, P2, P2 Cl, P3 and P3 Cl. Samples labelled with “Cl” was immersed into a solution of 0.01 molar solution of 4-Chloro-2-hydroxybenzaldehyde or 4-chloroaniline in MeOH.

No.	Length
1	112.361
2	113.219
3	105.709
4	73.323
5	99.732
6	73.951
7	90.591
8	111.611
9	111.051
Mean	**100.413**
SD	**17.830**

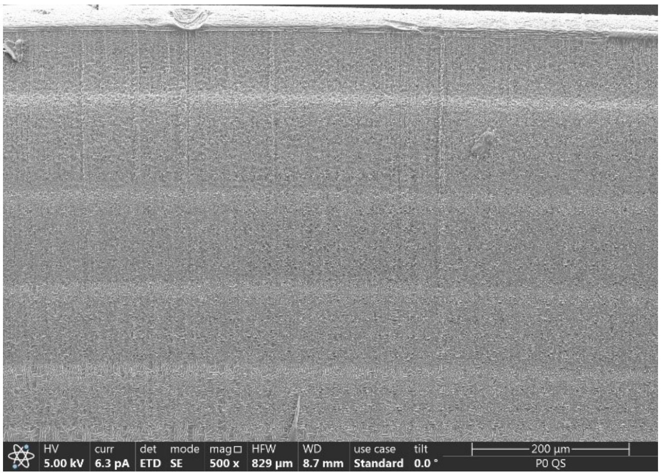


Figure S31: SEM picture and Measurements of the Layer Hight of the 3D printed polymer P0.

References

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