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Electronic Supplementary Information

for

Developing Non-Isocyanate Urethane-Methacrylate Photo-Monomers for 3D Printing Application

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1 Experimental

1.1 Materials

1,6-Hexanediamine (1,6-HDA, 99.5%), triethylamine (TEA, 99%), and propylene carbonate (PC, 99.5%) were bought from Acros Organics (Germany). 1,4-butanediol bis(3-aminopropyl) ether (1,4-BBE, 98%) was supplied by Alfa Aesar (Germany). n-Butylamine (n-BA, 99%), 4-(dimethyl-amino)pyridine (DMAP, 98%), and hydroquinone (HQ) were provided by Sigma Aldrich (Germany). Ethylene carbonate (EC, 99%), methacrylic anhydride (MAAn, 94%) were including bought from TCI (Germany). Other chemicals ethyl phenyl(2,4,6trimethylbenzoyl)phosphinate (TPO-L), dichloromethane (CH₂Cl₂, \geq 99%), anhydrous CH₂Cl₂ (\geq 99.9%), trichloromethane (CHCl₃, \geq 99%), anhydrous dimethylformamide (DMF, 99.8%), diethyl ether (Et₂O, ≥99%), sodium chloride (NaCl), potassium chloride (KCl), anhydrous magnesium sulfate (MgSO₄), hydrochloric acid (HCl), potassium hydroxide (KOH), sodium bicarbonate (NaHCO₃), disodium hydrogen phosphate (Na₂HPO₄), potassium dihydrogen phosphate (KH₂PO₄) were all analytical grade.

Phosphate-buffered saline (PBS) was prepared by dissolving NaCl (8.00 g), KCl (0.20 g), Na₂HPO₄ (1.44 g), and KH₂PO₄ (0.24 g) in distilled water (800 mL), adjusting the pH to 7.4 using HCl solution (0.1 M) or KOH solution (0.2 M) and adding distilled water to 1 L.

1.2 Synthesis of urethane-methacrylates1.2.1 Synthesis of UrDMA1

1,6-HDA (86.0 mmol, 1 eq.), EC (189.4 mmol, 2.2 eq.), and CH_2CI_2 (60 mL) were added in a round-bottomed flask and stirred at room temperature for 24 h.^{1,2} The precipitated product was filtered, washed three times with cold CH_2CI_2 , and dried in a vacuum oven at room temperature overnight. The product (**Urdiol1**) was a white powder (product yield: 93%, reaction yield 100% according to ¹H-NMR spectrum).



FTIR (1/λ, cm⁻¹): 3317 (O–H, v and N–H, v), 2941 and 2869 (C–H, v), 1679 (C=O, v), 1526 (N–H, δ and C–N, v), 1458 and 1337 (CH₂, δ), 1253 (C–N, v), 1135 (CO–O, v), 1042 (C–O, v).^{1,3} ¹H-NMR (DMSO-*d*₆, δ, ppm): 1.23 (m, CH₂, 4H), 1.37 (m, CH₂, 4H), 2.95 (m, CH₂NH, 4H), 3.52 (t, CH₂OH, 4H), 3.94 (t, CH₂OCONH, 4H), 4.66 (br, OH, 2H), 6.72 (br, NH, 0.3H) and 7.05 (t, NH, 1.7H) two conformers.^{1,3}

¹³C-NMR (DMSO-*d*₆, δ, ppm): 26.42 (CH₂), 29.85 (CH₂), 40.59 (CH₂NH), 59.95 (CH₂OH), 65.85 (CH₂OCONH), 156.72 (OCONH).¹

Urdiol1 (68.4 mmol, 1 eq.), DMAP (1.3 mmol, 0.02 eq.), HQ (100 mg), and anhydrous DMF (40 mL) were added in a round-bottomed flask in an ice-bath under Ar atmosphere. Then, TEA (189.6 mmol, 2.77 eq.) was dropwise added to the flask. Afterward, MAAn (164.16 mmol, 2.4 eq.) was dropwise added to the flask. The reaction mixture was stirred at room temperature for 24 h under Ar atmosphere.² After that, DMF was removed on a rotary evaporator at 20 °C and the product was washed with water (100 mL) three times, dried in a vacuum oven at room temperature overnight, and freeze-dried for 5 d. The product (**UrDMA1**) was a light yellow powder with a melting point (T_m) of 76 °C (product yield: 99%, reaction yield 100% according to ¹H-NMR spectrum).



FTIR (1/λ, cm⁻¹): 3317 (N–H, v), 3045 (=C–H, v), 2940 and 2870 (C–H, v), 1688 (C=O, v), 1527 (N–H, δ and C–N, v), 1444 and 1395 (CH₂, δ), 1262 (C–N, v), 1153 (CO–O, v), 1050 (C–O, v).² ¹H-NMR (DMSO-*d*₆, δ, ppm): 1.22 (m, CH₂, 4H), 1.36 (m, CH₂, 4H), 1.88 (s, CH₃, 6H), 2.94 (m, CH₂NH, 4H), 4.20 (t, CH₂OCONH, 4H), 4.25 (t, CH₂OCO, 4H), 5.69 and 6.03 (s, CH₂=C, 4H), 6.87 (br, NH, 0.3H) and 7.21 (t, NH, 1.7H) two conformers.²

¹³C-NMR (DMSO-*d*₆, δ, ppm): 18.38 (CH₃), 26.38 (CH₂), 29.76 (CH₂), 40.62 (CH₂NH), 61.96 (CH₂OCONH), 63.59 (CH₂OCO), 126.43 (CH₂=C), 136.14 (C=CH₂), 156.39 (OCONH), 166.88 (OCO).²

1.2.2 Synthesis of UrDMA2

1,6-HDA (86.0 mmol, 1 eq.), PC (189.4 mmol, 2.2 eq.), and CHCl₃ (30 mL) were added in a round-bottomed flask and stirred at 60 °C for 48 h. After removing CHCl₃ in a rotatory evaporator, the obtained viscous liquid was precipitated in Et₂O, washed with Et₂O three times, and dried in a vacuum oven at room temperature overnight. The product (**Urdiol2**) was a white solid (product yield: 30%, reaction yield 100% according to ¹H-NMR spectrum). Based on integration values for the ¹H-NMR spectrum, the ring-opening reaction was done through breaking the O–CO bond at both β -position (41%) and γ -position (59%) of the methyl group.



FTIR (1/λ, cm⁻¹): 3322 (O–H, v and N–H, v), 2932 and 2869 (C–H, v), 1679 (C=O, v), 1527 (N–H, δ and C–N, v), 1474 and 1340 (CH₂, δ), 1254 (C–N, v), 1136 (CO–O, v), 1050 (C–O, v). ¹H-NMR (DMSO- d_6 , δ, ppm): 1.04 (d, CH₃, 2.5H), 1.10 (d, CH₃, 3.5H), 1.22 (m, CH₂, 4H), 1.36 (m, CH₂, 4H), 2.94 (m, CH₂NH, 4H), 3.40 (m, CH₂OH, 2.4H), 3.77 and 3.81 (m, CH₂OCONH and CHOH, 2.5H), 4.62 (m, CHOCONH, 1.2H) 4.72 (m, OH, 2H), 6.98 (t, NH, 1.2H) and 7.07 (t, NH, 0.8H) two conformers.

¹³C-NMR (DMSO-*d*₆, δ, ppm): 17.41 (CH₃), 20.53 (CH₃), 26.42 (CH₂), 29.86 (CH₂), 40.55 (CH₂NH), 64.42 (CHOH), 64.87 (CH₂OH), 69.27 (CHOCONH), 71.11 (CH₂OCONH), 156.45, 156.73 (OCONH).

Urdiol2 (25 mmol, 1 eq.), DMAP (0.5 mmol, 0.02 eq.), HQ (50 mg), and anhydrous CH_2Cl_2 (20 mL) were added in a round-bottomed flask in an ice-bath under Ar atmosphere. Then, TEA (70 mmol, 2.8 eq.) was dropwise added to the flask. Afterward, MAAn (60 mmol, 2.4 eq.) was dropwise added to the flask. The reaction mixture was stirred at room temperature for 24 h under Ar atmosphere. After that, saturated NaCl solution (100 mL) was added to get a two-phase separated mixture. The bottom phase was collected and washed with HCL solution (1 M, 100 mL) three times, saturated NaHCO₃ solution (100 mL) three times, and saturated NaCl solution (100 mL), and dried over anhydrous MgSO₄. Finally, CH_2Cl_2 was removed on a rotary evaporator at 20 °C and the product was dried in a vacuum oven at room temperature overnight (product yield: 89%). The product (**UrDMA2**) was a viscous liquid with no T_m and a glass transition (T_g) at -57 °C.



FTIR (1/ λ , cm⁻¹): 3355 (N–H, v), 3055 (=C–H, v), 2935 and 2874 (C–H, v), 1706 (C=O, v), 1641 (C=C, v), 1527 (N–H, δ and C–N, v), 1450 and 1387 (CH₂, δ), 1248 (C–N, v), 1152 (CO–O, v), 1038 (C–O, v).

¹H-NMR (CDCl₃, δ, ppm): 1.18 (d, CH₃, 2.5H), 1.25 (d, CH₃, 3.5H), 1.32 (m, CH₂, 4H), 1.48 (m, CH₂, 4H), 1.94 (s, CH₃, 6H), 3.16 (m, CH₂NH, 4H), 3.91 and 4.13 (m, CH₂OCONH, 1.6H), 4.01 and 4.18 (m, CH₂OCO, 2.4H), 4.79 (m, CHOCO, 0.9H) 5.09 (m, CHOCONH, 1.2H), 5.58 and 6.12 (s, CH₂=C, 4H), 7.14 (m, NH, 2H).

¹³C-NMR (CDCl₃, δ , ppm): 16.84 and 17.92 (CH₃), 18.26 (CH₃C=CH₂), 26.24 (CH₂), 29.80 (CH₂), 40.77 (CH₂NH), 66.67 (CHOCONH), 68.44 (CH₂OCONH), 69.07 (CHOCO), 70.12 (CH₂OCO), 125.90 (CH₂=C), 136.00 (C=CH₂), 155.89 and 156.82 (OCONH), 167.06 (OCO).

1.2.3 Synthesis of UrDMA3

1,4-BBE (95.9 mmol, 1 eq.), EC (211.0 mmol, 2.2 eq.), and CHCl₃ (50 mL) were added in a round-bottomed flask and stirred at room temperature for 48 h. After removing CHCl₃ in a rotatory evaporator, the obtained viscous liquid was precipitated in Et_2O , washed with Et_2O (100 mL) three times, and was dried in a vacuum oven at room temperature overnight. The product (**Urdiol3**) was a white solid (product yield: 98%).



FTIR (1/ λ , cm⁻¹): 3313 (O–H, v) 3263 (N–H, v), 2949 and 2865 (C–H, v), 1681 (C=O, v), 1534 (N–H, δ and C–N, v), 1456 and 1371 (CH₂, δ), 1254 (C–N, v), 1105 (CO–O, v), 998 (C–O, v).

¹H-NMR (CDCl₃, δ, ppm): 1.63 (m, CH₂, 4H), 1.77 (m, CH₂, 4H), 3.18 (br, OH, 2H), 3.28 (m, CH₂NH, 4H), 3.50 (m, CH₂O, 8H), 3.78 (t, CH₂OH, 4H), 4.16 (t, CH₂OCONH, 4H), 5.28 and 5.56 (br, NH, 2H).

Urdiol3 (52.6 mmol, 1 eq.), DMAP (1 mmol, 0.02 eq.), HQ (100 mg), and anhydrous CH_2Cl_2 (60 mL) were added in a round-bottomed flask in an ice-bath under Ar atmosphere. Then, TEA (145.8 mmol, 2.8 eq.) was dropwise added to the flask. Afterward, MAAn (188.7 mmol, 2.4 eq.) was dropwise added to the flask. The reaction mixture was stirred at room temperature for 24 h under Ar atmosphere. After that, saturated NaCl solution (200 mL) was added to get a two-phase separated mixture. The bottom phase was collected and washed with HCl solution (1 M, 200 mL) three times, saturated NaHCO₃ solution (200 mL) three times, and saturated NaCl solution (200 mL), and dried over anhydrous MgSO₄. The CH_2Cl_2 was removed on a rotary evaporator at 20 °C and the product was dried in a vacuum oven at room temperature overnight. The product (UrDMA3) was a yellow waxy liquid, which slowly crystallized by cooling with a T_m of 31 °C (product yield: 74%).



FTIR (1/ λ , cm⁻¹): 3351 (N–H, v), 2942 and 2867 (C–H, v), 1711 (C=O, v), 1640 (C=C, v), 1526 (N–H, δ and C–N, v), 1448 and 1373 (CH₂, δ), 1246 (C–N, v), 1153 (CO–O, v), 1109 and 1054 (C–O, v).

¹H-NMR (DMSO-*d*₆, δ, ppm): 1.50 (m, CH₂, 4H), 1.61 (m, CH₂, 4H), 1.88 (s, CH₃, 6H), 3.02 (m, CH₂NH, 4H), 3.33 (t, CH₂O, 8H), 4.20 (t, CH₂OCONH, 4H), 4.25 (t, CH₂OCO, 4H), 5.69 and 6.03 (s, CH₂=C, 4H), 6.86 and 7.21 (br, NH, 2H).

¹³C-NMR (DMSO-*d*₆, δ, ppm): 18.38 (CH₃), 26.48 (CH₂), 30.08 (CH₂), 38.06 (CH₂NH), 62.01 (CH₂OCONH), 63.57 (CH₂OCO), 67.95 (CH₂O), 70.28 (CH₂O), 126.43 (CH₂=C), 136.14 (C=CH₂), 156.39 (OCONH), 166.76 (OCO).

1.2.4 Synthesis of UrMA1

n-BA (676.8 mmol, 1 eq.), EC (676.8 mmol, 1 eq.), and CH_2Cl_2 (100 mL) were added in a round-bottomed flask at 0 °C. The reaction was stirred at room temperature for 72 h.⁴ After removing CH_2Cl_2 in a rotatory evaporator, the product was dried in a vacuum oven at room temperature overnight. The product (**Urol1**) was a light yellow viscous liquid (product yield: 98%).



FTIR (1/λ, cm⁻¹): 3325 (O–H, v and N–H, v), 2943 and 2875 (C–H, v), 1691 (C=O, v), 1534 (N–H, δ and C–N, v), 1453 (CH₂, δ), 1248 (C–N, v), 1141 (CO–O, v), 1059 (C–O, v). ¹H-NMR (CDCl₃, δ, ppm): 0.91 (t, CH₃, 3H), 1.34 (m, CH₂, 2H), 1.47 (m, CH₂, 2H), 3.15 (t, CH₂NH, 2H and br, OH, 1H), 3.77 (t, CH₂OH, 2H), 4.17 (t, CH₂OCONH, 2H), 4.88 and 5.08 (br, NH, 1H). ¹³C-NMR (CDCl₃, δ, ppm): 13.70 (CH₃), 19.87 (CH₂), 31.92 (CH₂), 40.80 (CH₂NH), 61.66 (CH₂OH), 66.58 (CH₂OCONH), 157.08 (OCONH).

Urol1 (58.8 mmol, 1 eq.), DMAP (0.6 mmol, 0.01 eq.), HQ (52 mg), and anhydrous CH_2Cl_2 (20 mL) were added in a round-bottomed flask in an ice-bath under Ar atmosphere. Then, TEA (82.3 mmol, 1.4 eq.) was dropwise added to the flask. Afterward, MAAn (70.6 mmol, 1.2 eq.) was dropwise added to the flask. The reaction mixture was stirred at room temperature for 24 h under Ar atmosphere.⁴ After that, saturated NaCl solution (50 mL) was added to get a two-phase separated mixture. The bottom phase was collected, washed with HCl solution (1 M, 50 mL) three times, saturated NaHCO₃ solution (50 mL) three times, and saturated NaCl solution (50 mL), and dried over anhydrous MgSO₄. The CH_2Cl_2 was removed on a rotary evaporator at 20 °C and the product was dried in a vacuum oven at room temperature overnight. The product (**UrMA1**) was yellow liquid with a T_m of 3 °C (product yield: 82%).



FTIR (1/λ, cm⁻¹): 3354 (N–H, v), 2948 and 2876 (C–H, v), 1710 (C=O, v), 1639 (C=C, v), 1528 (N– H, δ and C–N, v), 1450 and 1387 (CH₂, δ), 1246 (C–N, v), 1153 (CO–O, v), 1050 (C–O, v).⁴ ¹H-NMR (CDCl₃, δ, ppm): 0.91 (t, CH₃, 3H), 1.34 (m, CH₂, 2H), 1.47 (m, CH₂, 2H), 1.94 (m, CH₃,

3H), 3.16 (m, CH₂NH, 2H), 4.31 (br, CH₂OCO, 2H and CH₂OCONH, 2H), 4.81 (br, NH, 1H), 5.58 and 6.12 (s, CH₂=, 2H).⁴

¹³C-NMR (CDCl₃, δ, ppm): 13.70 (CH₃), 18.26 (CH₃C=CH₂), 19.85 (CH₂), 31.96 (CH₂), 40.76 (CH₂NH), 62.41 (CH₂OCONH), 125.86 (CH₂=C), 135.99 (C=CH₂), 156.14 (OCONH), 167.18 (OCO). (OCO).

1.3 Photo-curing of urethane-methacrylates

For photo-curing of urethane-methacrylates, each monomer was mixed with TPO-L (3 wt%) as a photoinitiator. UrDMA1 was warmed up to melt before mixing with TPO-L. The mixtures were poured into Teflon or silicone molds (depth of 0.5 mm) and cured with a UV lamp (Hönle AG UV Technology, Bluepoint 4 ecocure) at 100% power for 60 s under an Ar atmosphere. The other side of cured samples was post-cured for another 60 s. All the cured samples were denoted with a prefix "X" following the name of the respective monomer. For example XUrDMA1 for cured sample based on UrDMA1 monomer.

1.4 3D printing of urethane-methacrylates

3D printability of the prepared monomers was evaluated on a digital light processing (DLP) printer (MiiCraft, MiiCraft Ultra 125x, Taiwan) operating at 365 nm. For this purpose, a mixture of prepared monomers containing TPO-L was used as ink (the formulation is not reported).

1.5 Instruments

Fourier-transform infrared (FTIR) spectroscopy of monomers and cured samples was done using a Digilab instrument (FTS 2000 Series, USA) equipped with an attenuated total reflection (ATR) unit.

A nuclear magnetic resonance (NMR) spectrometer (Varian, Unity Inova 500 NB, USA) was employed for recording the ¹H- and ¹³C-NMR spectra of monomers at 25 °C using CDCl₃ or DMSO- d_6 as solvents.

Differential scanning calorimetry (DSC) of monomers and cured samples was performed on a Netzsch device (DSC 204 F1 Phoenix, Germany) operating at a heating rate of 10 °C/min under N₂ atmosphere. For monomers, T_g (middle point of base-line change) and T_m (peak maximum) values were extracted from the first heating cycle. For evaluating photo-curing of monomers containing TPO-L (3 wt%), the DSC machine was equipped with a spot UV curing system (Lumen Dynamics, OmniCure[®] S2000, Canada) with an intensity of 1 W/m².

Dynamic mechanical analysis (DMA) of cured samples was done on a TA Instruments machine (DMA Q800, USA) running in single cantilever mode at a frequency of 1 Hz, an amplitude of 20 μ m, and over a temperature range of -50–200 °C with a heating rate of 3 °C/min. The specimens were prepared using a self-made flexible silicone mold. The glass transition temperature (Tg) was estimated from the peak of the tan δ curve.

A Mettler Toledo thermogravimetric analyzer (TGA 2, Germany) was used to study the thermal degradation of cured samples at a heating rate of 10 $^{\circ}$ C/min under N₂ atmosphere.

1.6 Methods

The gel content of cured samples was determined through extraction with acetone. For this purpose, samples (n=4) were dried in a vacuum oven at room temperature for 4 d, accurately weighed (m_1 , 210-490 mg), and extracted with acetone in a Soxhlet apparatus for 9 d. After that, the extracted samples dried in a vacuum oven at 40 °C for 3 d and again weighed (m_2). The gel content values were calculated according to Equation 1.

$$Gel\ content = \frac{m_2}{m_1} \times 100\tag{1}$$

The bulk hydrophilicity of cured samples was evaluated by measuring the water absorption in the PBS solution. To that end, samples (n=4) were dried in a vacuum oven at room temperature for 4 d, accurately weighed (m_1 , 240-560 mg), and immersed in PBS solution (30 mL) at 37 °C up to 7 d. After certain time intervals, the swollen samples were taken out, gently wiped by a paper towel to remove surface water, and immediately weighted (m_2). The water absorption values were calculated according to Equation 2:

Water absorption
$$= \frac{m_2 - m_1}{m_1} \times 100$$
 (2)

The photo-curing rate (R_p , 1/s) and double bond conversion (*DBC*, %) as a function of time were calculated from photo-DSC data using Equations 3-5. ⁵

$$\Delta H_{theor} = \frac{f \cdot n \cdot \Delta H_0}{M_W} \tag{3}$$

$$R_p = \frac{dH_p}{dt} / \Delta H_{theor} \tag{4}$$

$$DBC = \frac{\Delta H_p}{\Delta H_{theor}} \times 100 \tag{5}$$

where ΔH_{theor} (J/g) is the theoretical total heat released during the complete polymerization of the monomer within the sample, f is the mass fraction of the monomer within the sample, n is the number of double bonds in the monomer, ΔH_0 (J/mol) is the standard heat of polymerization for methacrylate (54.8 kJ/mol ^{2,6}), M_w (g/mol) is the molecular weight of the monomer, dH_p/dt (J/s·g or W/g) is the normalized heat flow per second, and ΔH_p (J/g) is the heat released from the start of photo-curing up to a certain time obtained from the integration of thermograms.

The crosslink density (v_c , mole number of network chains per unit volume) for cured samples was calculated from DMA data using Equation 6 from the statistical theory of rubber elasticity ⁷:

$$E' = \Phi \nu_c R T \tag{6}$$

where E' is the storage modulus in the rubbery region, Φ is the front factor assumed to be 3 for an ideal rubber, R is the gas constant, and T is the absolute temperature at the beginning of the rubbery plateau.

1793/A₂₉₂₈ 708/A2928 **Absorption Ratio** Time (h)

2 Results and Discussion

2.1 FTIR spectroscopy for reaction mixture of 1,6-HDA and PC

Figure S1. Monitoring the progress of the aminolysis reaction of PC with 1,6-HDA at 60 °C via FTIR spectroscopy. A₁₇₉₃, A₁₇₀₈, and A₂₉₂₈ are the absorbances for the peaks related to cyclic carbonate, urethane, and aliphatic alkyl moieties.

2.2 NMR spectroscopy for Urdiol2



Figure S2. ¹H-NMR (a) and ¹³C-NMR (b) spectra for Urdiol2 in DMSO-d₆.

2.3 NMR spectroscopy for Urdiol1



Figure S3. ¹H-NMR (a) and ¹³C-NMR (b) spectra for Urdiol1 in DMSO-d₆.

2.4 DSC for urethane-methacrylates



Figure S4. DSC thermograms for urethane-methacrylates at a heating rate of 10 °C/min under N₂ atmosphere.

2.5 Photo-DSC for urethane-methacrylates



Figure S5. Photo-DSC of urethane-methacrylates containing TPO-L (3 wt%) under N_2 atmosphere. The intensity of the UV lamp was 1 W/m².



Figure S6. DSC thermograms for cured samples at a heating rate of 10 °C/min under N_2 atmosphere.

2.7 Water absorption of cured samples in PBS



Figure S7. Water absorption of cured samples in PBS at 37 °C.



2.8 TGA for cured samples

Figure S8. TGA thermograms for cured samples at a heating rate of 10 °C/min under N_2 atmosphere.

2.9 3D printing of urethane-methacrylates



Figure S9. The model used during the 3D printing process. The copyright belongs to BURMS - 3D Druck Jena GmbH & Co.KG.

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