# **Supporting Information**

Photo-polymerizable, low shrinking modular construction kit with high efficiency based on vinylcyclopropanes

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### Supplementary Information according to Experimental Part

#### Complexness of isomeric structures for bi-functional VCP derivatives

The hydrolysis of the racemic 2-vinylcyclopropane-1,1-dicarboxylate results in a racemic mixture of diastereoisomers in a ratio of about 90:10. With continuing synthesis the isomeric complexity is passed on. To avoid losing a general overview over the basic monomer structure, only the most probable isomeric structure is presented within the main part of the manuscript. However, at this point an exemplary structural description of a VCP derivative is presented within Scheme S1.

Scheme S1. Exemplary structural description of the stereo centers and the isomeric complexity of VCP derivatives.



### Characterization of polypropyleneglycole Genamine D01/2000 end-capped with two ethyl 1-(carbamoyl)-2-vinylcyclopropanecarboxylate units (in this work abbreviated to VCPPPG2000)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.83-8.32$  (m, 2 H, NH), 5,70-5.55 (m, 2 H, CH=CH<sub>2</sub>), 5.34-5.26 (m, 2 H, CH=CHH), 5.15-5.11 (m, 2 H, CH=CHH), 4.24-4.02 (m, 2 H, NH-CH, 4 H, O-CH<sub>2</sub>), 3.77-3.23 (overlapping of proton signals: 3.77-3.60, m, O-CH<sub>2</sub>, 3.60-3.23, m, O-CH<sub>2</sub> and O-CH<sub>3</sub> of PPG repeat unit) 2.55-2.44 (m, 2H, CH-CH), 2.02-1.97 (m, 2H, -CHH), 1.83-1.79 (m, 2H, -CHH), 1.29-1.18 (overlapping of proton signals, m, 2 x 3H, -CH<sub>3</sub>), 1.18-1.00 (broad s, -CH<sub>3</sub> of PPG repeat unit); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 170.6$  (NH-C=O), 166.9 (O-C=O), 133.2 (CH=CH<sub>2</sub>), 119.0 (CH=CHH), 75.0 (O-CH<sub>2</sub>), 73.4-71.8 (backbone of PPG repeat unit), 61.0 (O-CH<sub>2</sub>), 45.4 (-CH), 36.2 (CH-CH), 34.0 (C<sub>4</sub>), 20.9 (>CHH), 18.0 (CH<sub>3</sub>), 17.1 (-CH<sub>3</sub> of PPG repeat unit), 13.9 (-CH<sub>3</sub>); FT-IR (attenuated total reflectance (ATR)): v = 3358 (w), 2971 (m), 2868 (m), 1707 (m), 1655 (m), 1526 (w), 1451 (m), 1373 (s), 1342 (m), 1298 (m), 1260 (w), 1098 (vs), 1015 (s), 920 (m), 864 (m), 833 (w), 733 (m); n<sub>D</sub><sup>20</sup> = 1.462; determined by DSC: glass transition temperature of monomer T<sub>g</sub> = -55 °C, determined by (MALDI-TOF-MS): M<sub>n</sub> = 2126 g mol<sup>-1</sup>, M<sub>w</sub> = 2146 g mol<sup>-1</sup>, PDI = 1.01.



Figure S1: <sup>1</sup>H NMR of VCPPPG2000 (CDCl<sub>3</sub>, 300 MHz).





Figure S3: Full MALDI-TOF MS spectrum (linear mode) with an enlargement of 2160-2320 m/z region of VCPPPG2000.



Figure S4: Enlargement of MALDI-TOF MS spectrum within the reflectron mode in the region of 2227-2235 m/z region confirms the structural identification of VCPPPG<sub>2000</sub>.

## Characterization of diethyl 1,1'-(1,4-phenylenebis(methylene))bis(azanediyl)bis-(oxomethylene)-bis(2-vinylcyclopropanecarboxylate) (in this work abbreviated to "VCP-pphenyl")

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.83-8.45$ (m, 2 H, NH), 7.32 – 7.22 (s, 4H, aromatic protons) 5.74-5.59 (m, 2 H, CH=CH<sub>2</sub>), 5.36-5.29 (m, 2 H, CH=CHH), 5.17-5.12 (m, 2 H, CH=CHH), 4.54-4.37 (m, 4 H, NH-CH<sub>2</sub>), 4.23-4.05 (m, 4 H, O-CH<sub>2</sub>), 2.62-2.53 (m, 2H, CH-CH), 2.10-2.04(m, 2H, >CHH), 1.90-1.85(m, 2H, >CHH), 1.26-1.22 (t, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 171.4$  (NH-C=O), 168.1(O-C=O), 137.6 (C<sub>arom</sub>), 133.4 (CH=CH<sub>2</sub>), 128.1 (C<sub>arom</sub>), 119.7 (CH=CHH), 61.6 (O-CH<sub>2</sub>), 43.8 (-CH<sub>2</sub>), 37.2 (CH-CH), 34.4 (C<sub>4</sub>), 21.6 (-CHH), 14.3 (-CH<sub>3</sub>); FT-IR (attenuated total reflectance (ATR)): v = 3345 (m), 3084 (w), 2983 (w), 2934 (w), 1703 (vs), 1647 (s), 1525 (vs), 1466 (w), 1429 (m), 1372 (m), 1335 (m), 1314 (s), 1196 (m), 1139 (vs), 1071 (w), 1018 (m), 995 (m), 957 (m), 915 (s), 856 (m), 831 (m), 775 (w), 752 (m), 623 (m), 573 (m); HRMS (ESI, pos.) m/z calculated for C<sub>26</sub>H<sub>32</sub>O<sub>6</sub>N<sub>2</sub> [M + H]<sup>+</sup> 469.2333, found 469.2331 and 491.2149 [M + Na]<sup>+</sup>; determined by DSC: glass transition temperature T<sub>g</sub> = -15 °C.



Figure S6: <sup>13</sup>C-NMR of VCP-p-phenyl (CDCl<sub>3</sub>, 75 MHz).

## Characterization of diethyl 1,1'-(1,3-phenylenebis(methylene))bis(azanediyl)bis-(oxomethylene)-bis(2-vinylcyclopropanecarboxylate) (in this work abbreviated to "VCP-mphenyl")

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.82-8.45$ (m, 2 H, NH), 7.32 – 7.17 (m, 4H, aromatic protons) 5.74-5.59 (m, 2 H, CH=CH<sub>2</sub>), 5.36-5.29 (m, 2 H, CH=CHH), 5.17-5.12 (m, 2 H, CH=CHH), 4.54-4.37 (m, 4 H, NH-CH<sub>2</sub>), 4.23-4.05 (m, 4 H, O-CH<sub>2</sub>), 2.62-2.53 (m, 2H, CH-CH), 2.10-2.04(m, 2H, >CHH), 1.90-1.85(m, 2H, >CHH), 1.26-1.22 (t, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 171.3$  (NH-C=O), 168.1(O-C=O), 138.8 (C<sub>arom</sub>), 133.3 (CH=CH<sub>2</sub>), 129.1 (C<sub>arom</sub>), 127.1 (C<sub>arom</sub>), 126.7 (C<sub>arom</sub>), 119.7 (CH=CHH), 61.5 (O-CH<sub>2</sub>), 43.9 (-CH<sub>2</sub>), 37.1 (CH-CH), 34.3 (C<sub>4</sub>), 21.6 (-CHH), 14.2 (-CH<sub>3</sub>); FT-IR (attenuated total reflectance (ATR)): v = 3353 (m), 3084 (w), 2983 (w), 2934 (w), 1703 (vs), 1653 (s), 1525 (vs), 1443 (m), 1372 (m), 1335 (w), 1312 (s), 1265 (w), 1198 (m), 1139 (vs), 1071 (w), 1019 (m), 993 (m), 958 (m), 914 (s), 862 (m), 833 (m), 772 (w), 733 (m), 702 (m), 644 (m); n<sub>D</sub><sup>20</sup> = 1.535; HRMS (ESI, pos.) m/z calculated for C<sub>26</sub>H<sub>32</sub>O<sub>6</sub>N<sub>2</sub> [M + H]<sup>+</sup> 469.2333, found 469.2331 and 491.2151 [M + Na]<sup>+</sup>; determined by DSC: glass transition temperature T<sub>g</sub> = -15 °C.



Figure S7: <sup>1</sup>H NMR of VCP-m-phenyl (CDCl<sub>3</sub>, 300 MHz).



Figure S8: <sup>13</sup>C-NMR of VCP-m-phenyl (CDCl<sub>3</sub>, 75 MHz).

#### **Supplementary Analytical Data**

#### Temperature variable FT-IR measurements (ATR measurements of bulk material)



**Figure S9:** Recorded FT-IR(ATR) spectra of VCP-m-phenyl between temperature ranges of 25 - 90 °C. Due to the temperature dependency of hydrogen bonds, with increased temperature these bonds are weakened and show an alteration in shape and shift. Thus, especially the N-H (3355 cm<sup>-1</sup>) and C=O (1652 cm<sup>-1</sup>) stretching vibration of the amide group shift to higher frequencies with increased temperature. Compared to UDMA the shift is less strong, as hydrogen bonds of urethane groups are general more strong than for amides, and secondly for UDMA a higher number of acceptor atoms is available (8 oxygen atoms).



**Figure S10:** Recorded FT-IR(ATR) spectra of VCPPPG<sub>2000</sub> between temperature ranges of 25 - 90 °C. Due to the temperature dependency of hydrogen bonds, with increased temperature these bonds are weakened and show an alteration in shape and shift. Thus, especially the N-H (3358 cm<sup>-1</sup>) and C=O (1656 cm<sup>-1</sup>) stretching vibration of the amide group shift to higher frequencies with increased temperature. Compared to VCP-mphenyl the shift of the signals to higher and lower frequencies is equally strong, which confirms that the strength of the hydrogen bonds of VCP-mphenyl and VCPPPG<sub>2000</sub> should be at near equal level. However, due the signal intensity of the functional groups of VCPPPG<sub>2000</sub> is lower, as the signals of the PPG macro-spacer account to the main IR-activity. Nevertheless the tendency is still visible.



**Figure S11:** Recorded FT-IR(ATR) spectra of UDMA between temperature ranges of 25 - 90 °C. Due to the temperature dependency of hydrogen bonds, with increased temperature these bonds are weakened and show an alteration in shape and shift. Thus, especially the N-H (3358 cm<sup>-1</sup>) and C=O (1702 cm<sup>-1</sup>) stretching vibration shift to higher frequencies with increased temperature. Rather non hydrogen bond affected functional groups are temperature independent and remain constant in their shift and shape.



**Figure S12:** A: Comparison of the thermal stability of cured VCPPPG<sub>2000</sub>, VCP-m/p-phenyl, UDMA, 1,12-DMA, DEGDMA and a mixture of BisGMA-TEGDMA in a ratio of 6:4 by TGA analysis, as well under nitrogen as protections gas as well under synthetic air (heating rate 10 K/min respectively). B: Determination of the maximum water uptake of the cured VCPPPG<sub>2000</sub>, VCP-m/p-phenyl, UDMA, 1,12-DMA, DEGDMA and BisGMA-TEGDMA\_6:4 samples by TGA measurements. The mass loss between 25-200°C determines the evaporation of absorbed water.

The oxidative degradation behavior of VCPPPG<sub>2000</sub> is due to the PPG spacer, and is in accordance with the literature.<sup>1</sup>

#### High resolution solid state <sup>13</sup>C-NMR spectroscopy of cured VCP ester-amides



**Figure S13:** <sup>13</sup>C-CP/MAS NMR (100MHz) of cured VCP-*p*-phenyl. The carbon atom of the terminal vinyl unit (CH2=CH-) at 119.7 ppm significantly disappeared after curing. The residual signal indicates the residual non cross-linked VCP-units. Compared to the cured VCP-*m*-phenyl the residual amount of non cross-linked VCP units seems to be slightly higher. However, still a quantification seems not possible, as the signal intensity is outside the current detection limit.



Further investigation of the partial crystallinity of VCP-p-phenyl

**Figure S14:** XRD measurements of VCP-p-phenyl. A: XRD diffractogram of VCP-p-phenyl at 25°C after purification, the characteristic XRD reflexes have been signed. B: Temperature dependent XRD measurements of VCP-p-phenyl to illustrate the melting behavior: The first diffractogram was measured at 25 °C, the second diffractogram was measured after heating at 90 °C, the crystalline phase melted completely as no further reflexes remained, the third diffractogram (25 °C a.m.) was measured after cooling the resin again to 25 °C (cooling rate ~5 K/min), no reflexes returned after cooling the resin, only two halos could be observed. After the VCP-p-resin is melted once, the recrystallization process is very slow, providing a partial recrystallization over weeks.

## References

1 L. Yang, F. Heatley, T. G. Blease, R. I. Thompson, *Eur. Polym. J.* 1996, **32**, 535.