Supporting Information

Synthesis of γ-cyclodextrin substituted bis(acyl)phosphane oxide derivative (BAPO-γ-CyD) serving as multiple photoinitiator and crosslinking agent

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Materials
γ-Cyclodextrin (Mn = 1297.14 g/mol) was purchased from ABCR. Acryloyl chloride, n-methyl pyrrolidone (NMP), Tetramethylguanidine (TMG), HCl in DEE, hydrogen peroxide (H₂O₂ 35%), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, 1,6 hexanediol diacrylate (HDDA, Mn = 226.27 g/mol) and poly(ethylene glycol) methyl ether methacrylate (PEGMEM, Mn = 500 g/mol) were obtained from Sigma Aldrich and used as received without further purification. Dimethoxyethane (DME) and toluene were degassed and purified using an Innovative Technologies PureSolv system.

Synthesis of acrylated-γCyclodextrin (Ac-γ-CyD, 3)
After being dried at 90 °C under high vacuum for 24 h, γ-CyD (20 g, 15.42 mmol, 1 eq.) was charged in a 500 mL round-bottom flask containing 160 mL of anhydrous n-methyl-pyrrolidone (NMP). The reaction mixture was stirred under protective atmosphere of Argon, till γ-CyD was totally dissolved. Then acryloyl chloride (36.07 mL, 0.44 mol, 28.8 eq.) was added dropwise at 0 °C. After stirring for 72 h at r.t. and 300 rpm, the reaction mixture was slowly dropped into 2 L of DI-H₂O to precipitate the product as a white powder. After decanting the mixture for 30 min. at r.t., Ac-γCyD (36.6 g, 67%) was filtered and washed four times using DI-H₂O. Finally, the product was dried for two days under high vacuum before being characterized by means of ¹H NMR, ¹³C{¹H} NMR, ATR-FTIR and MALDI-MS.

Synthesis of BAPO-γCyclodextrin (BAPO-γ-CyD, 5)
A solution of Ac-γ-CyD (2 g, 0.81 mmol, 1 eq.), bis(2,4,6-trimethylbenzoyl)hydrogenphosphane (BAP-H) (2.93 g, 8.9 mmol, 11 eq.) and TMG (0.11 mL, 0.89 mmol, 1.1 eq.) in 90 mL of DME was prepared in a 250 ml Schlenk flask. After stirring for 1 h at 300 rpm and 50 °C, the solvent was removed under reduced pressure. The yellow oily residue was dissolved in 90 mL of Toluene. After the addition of HCl (HCl in DEE, 0.45 mL, 0.89 mmol, 1.1 eq.) at r. t., the mixture was left to stir for 1 h and then filtered over celite. Then, aq. H₂O₂ (0.84 mL, 9.8 mmol, 12 eq., 35%) was added dropwise in the dark at 0 °C. After stirring vigorously at r.t. for 1 h, the solvent was removed under reduced pressure to yield BAPO-γ-CyD as a light-yellow powder (4.7 g, 95%). The product was dried for two days under high vacuum before being characterized by means of ¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR, ATR-FTIR and MALDI-MS; and then stored in the dark at 4 °C.

Solution NMR spectroscopy
¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR spectra were recorded on Bruker 500 spectrometer operating at 500.26 MHz, 125.80 MHz and 202.50 MHz, respectively. Chemical shifts δ were measured according to IUPAC and are given in parts per million (ppm) relative to TMS and H₃PO₄ for ¹H NMR, ¹³C{¹H} NMR and ³¹P{¹H} NMR.

ATR-FTIR spectroscopy
ATR spectra were recorded between 4000 and 600 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans per sample using a Tensor 27 FT-IR spectrometer (Bruker, Switzerland).

MALDI-MS
Mass spectrometry measurements were carried out by the MS Service (Laboratory of Organic Chemistry) at ETH Zürich.

UV-Vis spectroscopy
UV/vis spectra were recorded on a UV/vis/NIR lambda-19-spectrometer (range 200 - 600 nm) in 10 mm Quartz cells. The molar extinction coefficients (ε) were calculated using the following equation (S1.1):

\[ \varepsilon = \log \left( \frac{I}{I_0} \right) \frac{1}{cl} = \frac{A}{cl} \]  

where c is the concentration, l the extinction pathway (1 or 10 mm cuvette) and A is the absorption at 365 nm.

Photo-differential scanning calorimetry (Photo-DSC)
The tests were performed at 25 °C under N₂ atmosphere (30 mL/min), using a Mettler Toledo DSC. The light source was provided by a Hamamatsu LC8 lamp (cutoff filter under 400 nm, 0.6 mW/cm²) equipped with an 8 mm light guide. At the beginning of the measurements, an isothermal period of 120 s was scheduled before the irradiation was activated for 300 s. Subsequently, another isothermal period of 120 s was observed before the second irradiation period of
another 300 s was started. The DSC curve from the second irradiation period was subtracted from the first in order to provide a DSC curve, which excludes all thermal effects due to light dissipation. From the resulting DSC curves, the heat flux; \( t_{\text{onset}} \), the time to start the polymerization, \( t_{\max} \), the time to reach the maximum of heat flux, the double bond (C=C) conversion (DBC, S1.2) and the rate of conversion (Rp, S1.3) were obtained.

\[
DBC \% = \frac{\int_0^t \frac{dH}{dt} \cdot M_w}{\Delta H_T} \cdot 100 \quad S1.2
\]

\[
Rp = \frac{d(DBC)}{dt} = \frac{\frac{dH}{dt}}{\Delta H_T} \quad S1.3
\]

where \( M_w \) and \( \Delta H_T \) are the molecular weight and the theoretical heat of polymerization of the monomer (\( M_w,\text{HDDA} = 226.27 \text{ g/mol} \) and \( \Delta H_T,\text{HDDA} = 172 \text{ kJ/mol}^{[1,2]} \)).

**Photo-rheology**

Real-time photo-rheology measurements were performed using an Anton PAAR Modular Compact Rheometer (Physica MCR 302) in parallel-plate mode (25 mm diameter) and the visible-light source was provided by positioning the light guide of the Hamamatsu LCB lamp (6 mW/cm\(^2\)) under the bottom plate. During the measurements, the gap between the two glass plates was set to 0.2 mm and the sample was kept under a constant shear frequency of 1 Hz and strain amplitude of 1%. The irradiating light was switched on after 60 s to let the system stabilizing before the onset of polymerization. The kinetic of photopolymerization was studied as a function of the changes in the shear modulus (G') of the sample versus the exposure time. From the resulting curves, the delay (or induction) time (i.e. the irradiation time required to induce chemical crosslinking) and the slope of the curves (\( \Delta G' / \Delta t \), indication of the curing rate, measured in the first 30 s after \( t_d \)) can be obtained.

**Preparation of the samples**

Cylindrical samples were prepared by casting I, II, III and IV in a PDMS mold (0.75 cm diameter, 0.5 cm thick) and irradiating 4 min with visible light (Hamamatsu LCB, 8 mW/cm\(^2\)). All the samples were then postcured under UV light for 2 min and finally removed from the mold.

**Swelling ratio**

The samples were placed in deionized water for 24 h at r.t.. Then, the samples were removed from the water at different time interval and weighed after having wiped off the surface droplets with wet paper to gently remove excess water.\(^{[3]}\) The swelling degree (SW %) was measured gravimetrically using the following equation (S1.4):

\[
SW \% = \frac{W_t - W_0}{W_0} \cdot 100 \quad S1.4
\]

where \( W_t \) is the weight of the soaked sample at a certain time and \( W_0 \) is the initial weight of the dried sample. The water content of the samples at equilibrium (EWC) was also evaluated as follows (S1.5):

\[
EWC \% = \frac{W_t - W_0}{W_t} \cdot 100 \quad S1.5
\]

**Gel content measurements**

The gel content (insoluble fraction) of the products was determined following this procedure: the samples were first weighted and immersed in water for 24 hours at r.t. to dissolve the soluble fraction (non-cross-linked polymer) and
then dried for 24 h in a vacuum furnace (500 mbar, 70 °C). The gel content (GC) was calculated as weight difference before and after solvent extraction.\textsuperscript{[3]}
Characterization of acrylated-γ-Cyclodextrin (Ac-γ-CyD, 3)

Figure S1: $^1$H NMR of acrylated-γ-cyclodextrin (Ac-γ-CyD, 3) in DMSO.

Figure S2: $^{13}$C($^1$H) NMR of acrylated-γ-cyclodextrin (Ac-γ-CyD, 3) in DMSO.

Page S5
**Figure S3**: Comparison between the ATR-FTIR spectra of γ-cyclodextrin (γ-CyD, 1) and acrylated-γ-cyclodextrin (Ac-γ-CyD, 3).

**1H-NMR** (500.26 MHz, d6-DMSO, 298 K): δ ppm = 2.8 - 5.2 (H1, H2, H3, H4, H5, H6), 5.95 (-CH=CH$_2$), 6.18 (CH=CH$_2$) and 6.32 (-CH=CH$_2$).

**13C{1H}-NMR** (125.80 MHz, d6-DMSO, 298 K): δ ppm = 63.46 (C6), 69.39 (C5), 72.83 (C3), 73.18 (C2), 81.86 (C4), 102.13 (C1), 128.36 (-CH=CH$_2$), 132.06 (CH=CH$_2$) and 165.58 (-C=O).

**IR (ATR [cm$^{-1}$]):** 1727 (νC=O), 1633 (νC=C), 1410 (νH=CH=CH$_2$), 1297 cm$^{-1}$ (νC-O)unsat. α-β, 1156 cm$^{-1}$ (νC-O-glucopyran), 1080 cm$^{-1}$ (νC-O$_6$glucopyran), 1024 cm$^{-1}$ ([νC-C] + [νC-O])glucopyran and 809 (νC-H).

**Figure S4**: MALDI MS spectrum of acrylated-γ-cyclodextrin (Ac-γ-CyD, 3). The degree of substitution was calculated considering the average molecular weight of 3 (M$_w$ = 2450 g/mol), estimated from the normal distribution of the m/z peaks appearing in the MALDI spectrum. According to these data, 21 hydroxyl groups were acrylated on average.

**Characterization of BAPO-γCyclodextrin (BAPO-γ-CyD, 5)**

**Figure S5**: $^{31}$P{1H} NMR of BAPO-γ-cyclodextrin (BAPO-γ-CyD, 5) in DMSO.
Figure S6: $^1$H NMR of BAPO-γ-cyclodextrin (BAPO-γ-CyD, S) in DMSO.

Figure S7: $^{13}$C($^1$H) NMR of BAPO-γ-cyclodextrin (BAPO-γ-CyD, S) in DMSO.
Figure S8: Comparison between the ATR-FTIR spectra of acrylated-γ-cyclodextrin (Ac-γ-CyD, 2) and BAPO-γ-cyclodextrin (BAPO-γ-CyD, 5).

$^{31}$P{$^1$H} NMR (202.50 MHz, d6-DMSO, 298 K): δ [ppm] = 25.04 and 25.51

$^1$H-NMR (500.26 MHz, d6-DMSO, 298 K): δ [ppm] = 2.13 - 2.23 (s, 18 H, o-CH$_3$Mes and p-CH$_3$Mes), 2.65 (m, 4H, P-CH$_2$CH$_2$), 2.8 - 5.2 (H1, H2, H3, H4, H5, H6), 5.95 (−CH=CH$_2$), 6.18 (CH=CH$_2$), 6.32 (−CH=CH$_2$) and 6.77 (s, 4 H, H$_{2}$oMes).

$^{13}$C{$^1$H}-NMR (125.80 MHz, d6-DMSO, 298 K): δ [ppm] = 19.62 (s, o-CH$_3$Mes), 20.70 (s, p-CH$_3$Mes), 20.94 (s, -PCH$_2$CH$_2$), 25.58 (s, -PCH$_2$CH$_2$CO), 63.46 (C6), 69.39 (C5), 72.83 (C3), 73.18 (C2), 81.86 (C4), 100.13 (C1), 127.6 (s, C$_{3,5}$Mes), 128.36 (−CH=CH$_2$), 132.06 (CH=CH$_2$), 134.8 (s, C$_{2,6}$Mes), 137.0 (s, C$_7$Mes), 142.5 (d, C$_8$Mes), 165.58 and 216.54 (s, 1, COMes).

IR (ATR [cm$^{-1}$]): 1727 (νC=O), 1678 (νC=O), 1608 (νC$_{unsat}$), 1156 cm$^{-1}$ (νC-O-C)$_{glucopyran}$, 1143 (νP=O), 1080 cm$^{-1}$ (νC-O)$_{glucopyran}$, 1024 cm$^{-1}$ (νC-C) + (νC-O)$_{glucopyran}$, 853 and 796 (oop bending), 735 (νC-H bending) and 634 (νP-C). Rest peaks are attributed to residual acrylate groups.

UV/Vis $\lambda _{[nm]}$ = 300, 365, 400 (sh.).

MALDI MS of BAPO-γ-CyD (5): the degree of substitution was calculated considering the average molecular weight of 5 ($M_w = 5900$ g/mol), estimated from the normal distribution of the m/z peaks appearing in the MALDI spectrum. According to these data, about 10 bis(acyl)phosphane oxide units could be successfully grafted to 3.

References

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