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Supporting Information for

Synthesis and Hydrolytic Properties of Water-soluble Poly(carbonate-hydroxyurethane)s from Trimethylolpropane

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Figure S1 ¹H NMR spectrum of the mixture of TMP and 4 equiv. of DPC reacted at 140 °C for 132 h. Solvent: $CDCI_3$ with 0.03 (v/v)% of TMS.



Figure S2 ¹³C NMR spectrum of TMPC1 purified after isolated from the mixture of TMP and 4 equiv. of DPC reacted at 140 °C for 132 h. Solvent: DMSO-d₆.



Figure S3 NMR spectra of TMPC2 purified after isolated from the mixture of TMP and 4 equiv. of DPC reacted at 140 °C for 132 h. a) ¹H NMR spectrum in CDCl₃ with 0.03 (v/v)% of TMS. b) ¹³C NMR spectrum in DMSO-d₆.



Figure S4 NMR spectra of TMPC3 purified after isolated from the mixture of TMP and 4 equiv. of DPC reacted at 140 °C for 132 h. a) ¹H NMR spectrum in $CDCl_3$ with 0.03 (v/v)% of TMS. b) ¹³C NMR spectrum in DMSO-d₆.



Figure S5 Time course of mole fractions of TMP and TMPC in the mixture of TMP with 8 equiv. of DPC reacted at 140 °C. Red circles: TMP. Blue diamonds: TMPC2. Green triangles: TMPC3. Orange squares: TMPC1. Each line is added to easily understand.



Figure S6 ¹H NMR spectra of PCHUs (p(TMPC1-C₃)) synthesized by polyaddition of TMPC1 and equivalent of C₃ at the different temperature and reaction time. a) r. t., 64 h. b) 10 °C, 37 h. c) -10 °C, 46 h. d) -40 °C, 91 h. Solvent: DMSO-d₆ with a drop of acetic acid. Arrows show the signals originating from the cleavage of acyclic carbonate bonds. Signals based on the unreacted cyclic carbonate moieties are circled, which were used for the calculation of conversion of the polyaddition.

Calculation of polymerization degree and theoretical M_n of PCHUs and long-chained PCHUs

Polymerization degree (n) of PCHUs with respect to TMPC1-C₃ unit was calculated using the following equation.

$$2n = 1/(1 - p/100)$$

where r is the mole ratio of TMPC1 and C₃ (C₃/TMPC1) and p is the conversion of TMPC1 which were estimated from the change in proton ratio of methylene signals adjacent to cyclic and acyclic carbonate bonds at ca. 4.3 ppm. Theoretical M_n ($M_{n,theor}$) of PCHUs synthesized from TMPC1 with an equimolar of C₃ (r = C₃/TMPC1 = 1.00) was determined by the following equation.

 $M_{n,theor}$ = M.W. of TMPC1-C₃ unit x n = 420.45n (g mol⁻¹).

In the case of PCHUs synthesized from DTMPC1 and 1.25 equiv. of C_3 (r = 1.25), n and $M_{n,theor}$ were calculated using the following equations.

2n + 1 = (1 + 1/r)/(2(1 - p/100)/r + (1 - 1/r))

 $M_{n,theor}$ = M.W. of TMPC1-C₃ unit x n + M. W. of chain ends = 420.45n + 73.12 + 1.01 (g mol⁻¹). At the conversion of TMPC1 of 100% (p = 100), n is calculated to be 4.0 and then $M_{n,theor}$ is determined to be 1755.93 (g mol⁻¹).

n and $M_{n,theor}$ of long-chained PCHUs (p(TMPC1-C₃-Xy)) synthesized from TMPC1 and 1.25 equiv. of C₃ and 0.2 equiv. of Xy (TMPC1/C₃/Xy = 1/1.25/0.2 and r = NH₂/NCS = 1.25) were calculated by the following equation.

$$2n + 1 = (1 + 1/r)/(2(1 - p/100)/r + (1 - 1/r))$$

 $M_{n,\text{theor}} = M.W.$ of TMPC1-C₃-Xy unit x n + M. W. of chain ends = 1976.24n + 1754.92 + 1.01 (g mol⁻¹) Here, it was assumed that the reaction of TMPC1 and 1.25 equiv. of C₃ were completed to form p(TMPC1-C₃) ($M_{n,\text{theor}} = 1755.93$ (g mol⁻¹)). When the conversion of NCS groups of Xy is 100% (p = 100), n is calculated to be 4.0 and then $M_{n,\text{theor}}$ is determined to be 9660.89 (g mol⁻¹).





Chemical shift / ppm

Figure S7 ¹H NMR spectra of PCHUs ($p(TMPC1-C_3)$) before/after carboxylation. a) $p(TMPC1-C_3)$ in DMSO-d₆. The PHUCs were synthesized from the solution of TMPC1 and C₃ with a C₃/TMPC1 feed ratio of 1.25 at -10 °C for 48 h. The aliquot of the solution was measured after a drop of acetic acid was added. b) $p(TMPC1-C_3-Suc)$ in CD₃OD. Asterisks show residual solvents (DMF, EtOAc or acetone). The signal labelled as e' denotes

the methylene protons adjacent to the non-reacted hydroxyl groups.



Figure S8 ¹H NMR spectra of long-chained PCHUs ($p(TMPC1-C_3-Xy)$ before/after carboxylation. a) $p(TMPC1-C_3-Xy)$ in DMSO-d₆. The PCHUs were synthesized from the solution of TMPC1, C₃ and Xy with a C₃/TMPC1/Xy feed ratio of 1.25/1/0.2 at -10 °C. The aliquot of the solution was measured after a drop of acetic acid was added. b) $p(TMPC1-C_3-Xy-Suc)$ in CD₃OD. Asterisks show residual solvents (DMF, EtOAc or

acetone). The signal labelled as e' denotes the methylene protons neighboring to the non-reacted hydroxyl groups.



Figure S9 Comparison between FT-IR spectra. a) diisothiocyanate (Xy). b) carboxylated long-chained PCHUs ($p(TMPC1-C_3-Xy)$).



Figure S10 Characterization of hydrolytic properties of water-soluble PHUs (pDTMPC-C₃-SucNa) in 500 mM carbonate buffers at pH 10.6 and ambient temperature. A line is added to easily understand.