Supporting Information

Solubility-governed architectural design of polyhydroxyurethane-graft-poly(ϵ -

caprolactone) copolymers

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Figure S1. NMR spectra of pure DGC recorded in DMSO-d₆, ¹H (top, 400 MHz) and ¹³C (bottom, 100 MHz).

Sample	Catalyst	CL:OH:Catalyst	CL (g)	PHU (mg)	Catalyst (mg)	
CL100MSA0.05	MSA	100:1:0.05	3.25	50	1.37 (~1 μL)	
$CL_{100}MSA_1$	MSA	100:1:1	3.25	50	27.3 (18.5 μL)	
$CL_{100}MSA_3$	MSA	100:1:3	3.25	50	82 (55.5 μL)	
$CL_{100}Sn_{0.01}$	Sn(Oct) ₂	100:1:0.01	3.25	50	1.15	
$CL_{100}Sn_{0.02}$	Sn(Oct) ₂	100:1:0.02	3.25	50	2.30	
$CL_{100}Sn_{0.05}$	Sn(Oct) ₂	100:1:0.05	3.25	50	5.77	
$CL_{100}Sn_1$	Sn(Oct) ₂	100:1:1	3.25	50	115	
$CL_{10}Sn_{0.02}$	Sn(Oct) ₂	10:1:0.02	0.65	100	4.61	
$CL_{25}Sn_{0.02}$	Sn(Oct) ₂	25:1:0.02	0.81	50	2.30	
$CL_{50}Sn_{0.02}$	Sn(Oct) ₂	50:1:0.02	1.62	50	2.30	

Table S1. Mass of reactants used for monitoring the reaction kinetics.

Table S2. Mass of reactants used for the synthesis of the PHU–*graft*–PCL_x copolymers under the optimized conditions.

Х	CL:OH:Sn(Oct) ₂	CL (g)	PHU (mg)	$Sn(Oct)_2(mg)$
10	10:1:0.02	4	615	28.4
25	25:1:0.02	4	264	12.1
50	50:1:0.02	4	123	5.7
100	100:1:0.02	4	61.5	2.8



Figure S2. ³¹P NMR spectrum (CDCl₃) of the EDOBA PHU after phosphitylation with Cl-TMDP.

Calculation of solubility parameters

The solubility parameters of CL, BuOAc and the repeating units of the EDOBA and mXDA PHUs, were estimated based on Hoy's method of group contribution,^{1–4} Table S3.

Table S3.	Calculated solubility	parameters based	on Hoy's m	ethod of group	contribution.
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Substance	Group	N_i	$\mathbf{F}_{t,i}$	$\mathbf{F}_{\mathbf{p},\mathbf{i}}$	Vi	$\Delta_{\mathrm{T},i}^{(P)}$	α	n	$\boldsymbol{\delta}_t$	δ_p	δ_{h}	$\boldsymbol{\delta}_d$
	contribution		(MJ m ⁻³) ^{1/2} mol ⁻¹	(MJ m ⁻³) ^{1/2} mol ⁻¹	(cm ³				(MJ	(MJ	(MJ	(MJ
					mol ⁻¹)				m-	m-	m-	m-
									³) ^{1/2}	³) ^{1/2}	³) ^{1/2}	³) ^{1/2}
EDOBA	-COO-	1	640	528	23.7	0.047	1.40	0.96	25.5	17.2	13.7	12.8
PHU												
	-CH ₂ -	10	269	0	15.55	0.02						
	>CH-	2	176	0	9.56	0.013						
	-OH (H-	2	485	485	10.65	0.034						
	bonding)											
	-0-	3	235	216	6.45	0.018						
	-OCONH-	1	1265	890	34.8	0.094						
	-NH-	1	368	368	11	0.0275						
CL	-COO-	1	640	528	23.7	0.047	1.17	3.24	21.3	17.9	8.3	7.9
	-CH ₂ -	5	269	0	15.55	0.02						
	7-membered	1	92	0	0	0.007						
	ring											
BuOAc	-COO-	1	640	528	23.7	0.047	1.03	3.31	18.8	16.7	3.4	7.8
	-CH ₂ -	3	269	0	15.55	0.02						
	-CH ₃	2	303.5	0	21.55	0.022						

The equations applied for the calculation of the above parameters are as follows⁴:

$$\begin{split} F_t &= \sum N_i F_{t,i} \qquad F_p = \sum N_i F_{p,i} \qquad V = \sum N_i V_i \qquad \Delta_{\mathrm{T}}^{(p)} = \sum N_i \Delta_{\mathrm{T},i}^{(p)} \\ \alpha &= \frac{777 \ \Delta_{\mathrm{T}}^{(p)}}{V} \qquad n = \frac{0.5}{\Delta_{\mathrm{T}}^{(p)}} \\ \delta_t &= \frac{F_t + \frac{B}{n}}{V} \qquad \delta_p = \delta_t \left(\frac{F_p}{\alpha F_t + \frac{B}{n}}\right)^{\frac{1}{2}} \qquad \delta_h = \delta_t \left(\frac{\alpha - 1}{\alpha}\right)^{\frac{1}{2}} \qquad \delta_d = \left(\delta_t^2 - \delta_p^2 - \delta_h^2\right)^{\frac{1}{2}} \end{split}$$

where B is the base value equal to 277.

The solubility was determined based on the difference of the solubility parameters between the EDOBA PHU and CL or BuOAc through equation:

$$\Delta \delta = \left[(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2 \right]^{\frac{1}{2}}$$

where P and S stand for polymer (EDOBA PHU) and solvent (CL or BuOAc), respectively.



Figure S3. Ball-and-stick models of CL (a, b) and BuOAc (c, d) showing the difference of the alkyl groups in the ring vs. the linear form (hydrogens have been omitted for clarity).



Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃) of a PHU-CL mixture with 100:1 CL:OH ratio and no catalyst added, at 110 $^{\circ}$ C after 8 h. The conversion of CL to PCL due to thermal polymerization is 4.7%.



Figure S5. Elugrams of a) $CL_{100}MSA_1$, b) $CL_{100}MSA_3$ and c) $CL_{100}MSA_{0.05}$ at different times showing the difference in bimodality among them.



Figure S6. Elugrams of a) $CL_{100}Sn_{0.01}$, b) $CL_{100}Sn_{0.02}$ and c) $CL_{100}Sn_{0.05}$ and d) $CL_{100}Sn_1$ at different times showing the difference in bimodality among them.



Figure S7. Stacked ¹H NMR spectra of the $CL_{100}MSA_1$ sample after 30 min of reaction time, (a) as obtained and after fractionation through SEC (b) 1st peak, (c) 2nd peak. The inset graphs show some characteristic signals belonging to different adducts.



l86 184 182 180 178 176 174 172 170 168 166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 f1 (ppm)

Figure S8. Stacked ³¹P NMR spectra of the purified copolymers synthesized with varying MSA

and Sn(Oct)₂ content, respectively, compared to the pure EDOBA PHU and a non-grafted PCL.



Figure S9. Elugrams of a) $CL_{10}Sn_{0.02}$, b) $CL_{25}Sn_{0.02}$ and c) $CL_{50}Sn_{0.02}$ showing the broader distribution with decreasing CL loading.



Figure S10. Typical DSC curves (cooling and 2nd heating scan) of the PHU-graft-PCL copolymers.

References

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