

Supplementary Information

Synthesis and characterization of macrodiols and non-segmented poly(ester-urethanes) derived from α,ω -hydroxy telechelic poly(ϵ -caprolactone) (HOPCLOH). Effect of initiator, degree of polymerization, and diisocyanate

Miriam P. Barrera-Nava¹, Rodrigo Navarro², Ángel Marcos-Fernández², José E. Báez^{1*}

¹ Department of Chemistry, University of Guanajuato (UG), Noria Alta S/N, 36050 Guanajuato, Gto, Mexico.

² Institute of Polymer Science and Technology, CSIC, C/Juan de la Cierva No. 3, 28006 Madrid, Spain.

*Correspondence to: José E. Báez. Email: jebaez@ugto.mx

Table of contents

Tables	Page
Table S1. Poly(ϵ -caprolactone) diols (HOPCLOH) prepared using different types of linear aliphatic diols [HO(CH ₂) _m OH, where m=4, 8, and 12] as initiators in the ROP of CL. ^a	4
Table S2. Poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and three different types diisocyanates (HDI, MDI, and HMDI).	5
Table S3. Number-average molecular weight obtained by two different techniques of the HOPCLOH prepared using different types of linear aliphatic diols [HO(CH ₂) _m OH, where m=4, 8, and 12] as initiators in the ROP of CL. ^a	6
Table S4. Complete thermal properties of poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and three different types diisocyanates (HDI, MDI, and HMDI). Effect of the number of methylenes in HOPCLOH on the PEU. ^a	7
Table S5. Mechanical properties of poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and three different diisocyanates (HDI, MDI, and HMDI). Effect of the number of methylenes in HOPCLOH on the PEU. ^a	9
Figures	
Fig. S1. ¹³ C NMR (100 MHz) spectrum in CDCl ₃ at room temperature for PEU _{4a10A} .	10
Fig. S2. ¹³ C NMR (100 MHz) spectrum in CDCl ₃ at room temperature for PEU _{4a10B} .	11
Fig. S3. ¹³ C NMR (100 MHz) spectrum in CDCl ₃ at room temperature for PEU _{4a10C} .	12
Fig. S4. MALDI-TOF spectrum (linear mode) expanded view for the 1000–2000 m/z fragments of HOPCL _{4a10} OH (note: 114 and 16 are the values of the molecular weight of CL and the difference between Na ⁺ and K ⁺ (doping the same species of polymer), respectively).	13
Fig. S5. MALDI-TOF spectrum (linear mode) expanded view for the 1000–2000 m/z fragments of HOPCL _{8a10} OH (note: 114 and 16 are the values of the molecular weight of CL and the difference between Na ⁺ and K ⁺ (doping the same species of polymer), respectively).	14
Fig. S6. Effect of number of methylenes on the crystallinity PCL for poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and 1,6-hexamethylene diisocyanate (HDI). The PEUs derived from the macrodiols with DP=5 as initiator are indicated with open squares □, and macrodiols are indicated with	15

filled square ■ ; PEUs derived from macrodiols with DP=10 as initiator are indicated with open circles ○, and macrodiols are indicated with filled circles ●, and PEUs derived from macrodiols with DP=15 as initiator are indicated with open triangles △, and macrodiols are indicated with filled triangle▲.

Fig. S7. Effect of Hard Segment (HS) content on the crystallinity PCL for poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and 1,6-hexamethylene diisocyanate (HDI). The PEUs derived from the macrodiols with HO(CH₂)₄OH as initiator are indicated with squares (◻ DP=5; ◻ DP=10, and ◼ DP=15); PEUs derived from macrodiols with HO(CH₂)₈OH as initiator are indicated with circles (⊕ DP=5, ○ DP=10, and ● DP=15) and PEUs derived from macrodiols with HO(CH₂)₁₂OH as initiator are indicated with triangles (△ DP=5, △ DP=10, and ▲ DP=15).

16

Fig. S8. Mechanical properties of the synthesized PEUs with HDI: a) stress at break, b) strain at break, and c) modulus. The PEUs derived from the macrodiols with HO(CH₂)₄OH as initiator are indicated with squares (◻ DP=5; ◻ DP=10, and ◼ DP=15); PEUs derived from macrodiols with HO(CH₂)₈OH used as initiator are indicated with circles (⊕ DP=5, ○ DP=10, and ● DP=15) and PEUs derived from macrodiols with HO(CH₂)₁₂OH as initiator are indicated with triangles (△ DP=5, △ DP=10, and ▲ DP=15).

17

Table S1. Poly(ϵ -caprolactone) diols (HOPCLOH) prepared using different types of linear aliphatic diols $[\text{HO}(\text{CH}_2)_m\text{OH}]$, where $m=4, 8,$ and $12]$ as initiators in the ROP of CL.^a

DP (calcd)	Initiator		
	1,4-BD ^b	1,8-OD ^c	1,12-DD ^d
5	HOPCL _{4a5} OH	HOPCL _{8a5} OH	HOPCL _{12a5} OH
10	HOPCL _{4a10} OH	HOPCL _{8a10} OH	HOPCL _{12a10} OH
15	HOPCL _{4a15} OH	HOPCL _{8a15} OH	HOPCL _{12a15} OH

^aPolymerization at 150°C for 90 min with 65 mmol of CL, three CL/initiator molar ratios of 5,10, and 15 were used in the experiments ($\text{DP}_{(\text{calcd})}=5, 10,$ or 15) and ammonium decamolybdate as a catalyst. HOPCLOH= HO – PCL – OH or HO – $(\text{CH}_2)_m$ – PCL – OH, where $m = 4, 8,$ and 12 .

^b1,4-Butanediol

^c1,8-Octanediol

^d1,12-Dodecanediol

Table S2. Poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and three different types diisocyanates (HDI, MDI, and HMDI).

Diisocyanate	1,4-BD		
	HOPCL _{4a5} OH	HOPCL _{4a10} OH	HOPCL _{4a15} OH
HDI	PEU _{4a5A}	PEU _{4a10A}	PEU _{4a15A}
MDI	PEU _{4a5B}	PEU _{4a10B}	PEU _{4a15B}
HMDI	PEU _{4a5C}	PEU _{4a10C}	PEU _{4a15C}
Diisocyanate	1,8-OD		
	HOPCL _{8a5} OH	HOPCL _{8a10} OH	HOPCL _{8a15} OH
HDI	PEU _{8a5A}	PEU _{8a10A}	PEU _{8a15A}
MDI	PEU _{8a5B}	PEU _{8a10B}	PEU _{8a15B}
HMDI	PEU _{8a5C}	PEU _{8a10C}	PEU _{8a15C}
Diisocyanate	1,12-DD		
	HOPCL _{12a5} OH	HOPCL _{12a10} OH	HOPCL _{12a15} OH
HDI	PEU _{12a5A}	PEU _{12a10A}	PEU _{12a15A}
MDI	PEU _{12a5B}	PEU _{12a10B}	PEU _{12a15B}
HMDI	PEU _{12a5C}	PEU _{12a10C}	PEU _{12a15C}

Table S3. Number-average molecular weight obtained by two different techniques of the HOPCLOH prepared using different types of linear aliphatic diols [HO(CH₂)_mOH, where m=4, 8, and 12] as initiators in the ROP of CL.^a

Sample	Initiator	Alkyl(%) ^{b,c}	Conv(%) ^b	DP(calcd)	<i>M_n</i> (calcd) ^d	<i>M_n</i> (NMR) ^{d,e}	<i>M_n</i> (SEC) ^f	<i>M_w</i> / <i>M_n</i> ^f	Ratio ^g
HOPCL _{4a5} OH	HO(CH ₂) ₄ OH	16	98	5	650	570	1868	1.23	0.38
HOPCL _{4a10} OH	HO(CH ₂) ₄ OH	8	98	10	1230	1120	2575	1.33	0.48
HOPCL _{4a15} OH	HO(CH ₂) ₄ OH	5	99	15	1760	1660	3300	1.37	0.53
HOPCL _{8a5} OH	HO(CH ₂) ₈ OH	23	99	5	710	640	1819	1.19	0.39
HOPCL _{8a10} OH	HO(CH ₂) ₈ OH	12	99	10	1300	1210	2585	1.33	0.50
HOPCL _{8a15} OH	HO(CH ₂) ₈ OH	9	99	15	1750	1630	3184	1.36	0.55
HOPCL _{12a5} OH	HO(CH ₂) ₁₂ OH	29	99	5	770	690	1849	1.18	0.41
HOPCL _{12a10} OH	HO(CH ₂) ₁₂ OH	16	99	10	1350	1250	2651	1.32	0.51
HOPCL _{12a15} OH	HO(CH ₂) ₁₂ OH	11	99	15	1910	1780	3716	1.39	0.51

^aPolymerization at 150°C for 90 min with 65 mmol of CL, three CL/initiator molar ratios of 5,10, and 15 were used in the experiments (DP_(calcd)=5, 10, or 15) and ammonium decamolybdate as a catalyst. HOPCLOH= HO – PCL – OH or HO – (CH₂)_m – PCL – OH, where m = 4, 8, and 12.

^bDetermined by ¹H NMR in CDCl₃.

^cObtained from the equation alkyl (%) = (MW_{initiator}/M_n(NMR)) x 100, where MW_{initiator} is the molecular weight of initiator or alkyl diol (HOROH).

^dObtained from the equation *M_n*(calcd) = (MW(CL))(mmol CL/mmol ROH) + MW(HOROH), where MW is the molecular weight of ε-caprolactone monomer or aliphatic diol (HOROH).

^eObtained from the equation *M_n*(NMR) = (DP_(PCL) x MW(CL)) + MW(ROH), where MW is the molecular weight of ε-caprolactone monomer or aliphatic diol (HOROH).

^fDetermined by SEC results.

^g*M_n*(calcd)/*M_n*(SEC) ratio.

Table S4. Complete thermal properties of poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and three different types diisocyanates (HDI, MDI, and HMDI). Effect of the number of methylenes in HOPCLOH on the PEU.^a

Sample	Precursor	HS (%) ^{b,d}	SS (%) ^{b,d}	T_g (°C) ^e	T_c (°C) ^e	T_m (°C) ^e	ΔH_m (J/g) ^e	ΔH_{mpCL} (J/g) ^f	χ_i (%) ^g	Alkyl (%) ^h
PEU _{4a5} A	HOPCL _{4a5} OH	24	76	-49	-	51	10	10	7	16
PEU _{4a10} A	HOPCL _{4a10} OH	14	86	-57	-	31	15	15	11	8
PEU _{4a15} A	HOPCL _{4a15} OH	10	90	-57	-	43	29	29	22	5
PEU _{8a5} A	HOPCL _{8a5} OH	23	77	-49	-	51	13	10	7	23
PEU _{8a10} A	HOPCL _{8a10} OH	13	87	-58	-	30	19	16	12.5	12
PEU _{8a15} A	HOPCL _{8a15} OH	10	90	-61	-	41	31	28	20	9
PEU _{12a5} A	HOPCL _{12a5} OH	22	78	-47	-	58	15	12	9	29
PEU _{12a10} A	HOPCL _{12a10} OH	13	87	-58	-	36	19	16	12	16
PEU _{12a15} A	HOPCL _{12a15} OH	10	90	-58	-	46	29	26	19	11
PEU _{4a5} B	HOPCL _{4a5} OH	33	67	-17	-	-	-	-	-	16
PEU _{4a10} B	HOPCL _{4a10} OH	20	80	-40	-	-	-	-	-	8
PEU _{4a15} B	HOPCL _{4a15} OH	14	86	-48	-3	35	25	25	18	5
PEU _{8a5} B	HOPCL _{8a5} OH	31	69	-14	-	-	-	-	-	23
PEU _{8a10} B	HOPCL _{8a10} OH	19	81	-41	-	-	-	-	-	12
PEU _{8a15} B	HOPCL _{8a15} OH	15	85	-46	-1	29	13	11	8	9
PEU _{12a5} B	HOPCL _{12a5} OH	29	71	-18	-	-	-	-	-	29
PEU _{12a10} B	HOPCL _{12a10} OH	18	82	-41	-	13	1	1	1	16
PEU _{12a15} B	HOPCL _{12a15} OH	14	86	-49	-12	33	24	21	16	11
PEU _{4a5} C	HOPCL _{4a5} OH	33	67	-22	-	-	-	-	-	16
PEU _{4a10} C	HOPCL _{4a10} OH	21	79	-49	-	-	-	-	-	8
PEU _{4a15} C	HOPCL _{4a15} OH	15	85	-54	3	37	20	20	15	5
PEU _{8a5} C	HOPCL _{8a5} OH	30	70	-28	-	35	1	1	1	23
PEU _{8a10} C	HOPCL _{8a10} OH	19	81	-50	-	-	-	-	-	12
PEU _{8a15} C	HOPCL _{8a15} OH	15	85	-54	2	31	6	5	4	9
PEU _{12a5} C	HOPCL _{12a5} OH	29	71	-29	-	-	-	-	-	29
PEU _{12a10} C	HOPCL _{12a10} OH	19	81	-49	-	21	2	2	1	16
PEU _{12a15} C	HOPCL _{12a15} OH	14	86	-56	-31	34	27	24	18	11

HOPCLOH, α,ω -hydroxy telechelic poly(ϵ -caprolactone); PCL, poly(ϵ -caprolactone); PEU, poly(ester-urethane); HS, hard segment; SS, soft segment; A, 1,6-hexamethylene diisocyanate (HDI); B, methylene diphenyl diisocyanate (MDI); C, 4,4'-methylenebis (cyclohexyl isocyanate) (HMDI)). DSC, differential scanning calorimetry.

^aHOPCLOH = HO – PCL – OH or HO – (CH₂)_m – PCL – OH, where m = 4, 8, and 12.

^bHard segment.

^cSoft segment.

^dWeight percent.

^eObtained by DSC analysis.

^fCalculated from the equation $\Delta H_{mPCL} = \Delta H_m \cdot X_{SS}$ where X_{SS} is the weight fraction of soft segment in the HOCLOH oligoester.

^gQuantified from ΔH_m .

^hCalculated with respect to the HOPCLOH precursor. Percent determined by ¹H NMR in CDCl₃. Calculated from the equation $\text{alkyl (\%)} = (MW_{\text{initiator}}/M_n(\text{NMR})) \times 100$, where $MW_{\text{initiator}}$ is the molecular weight of initiator or alkyl diol (HOROH).

Table S5. Mechanical properties of poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and three different diisocyanates (HDI, MDI, and HMDI). Effect of the number of methylenes in HOPCLOH on the PEU.^a

Sample	Precursor	Stress at break (MPa)	Strain at break (%)	Modulus (MPa)	χ_i (%) ^b
PEU _{4a5} A	HOPCL _{4a5} OH	23.7 ± 1.70	948 ± 98	54.5 ± 3.0	7.0
PEU _{4a10} A	HOPCL _{4a10} OH	19.1 ± 1.39	1197 ± 13	2.9 ± 1.1	11.0
PEU _{4a15} A	HOPCL _{4a15} OH	23.6 ± 3.32	1503 ± 148	5.9 ± 5.3	22.0
PEU _{8a5} A	HOPCL _{8a5} OH	31.4 ± 2.06	1399 ± 101	89.9 ± 8.2	7.0
PEU _{8a10} A	HOPCL _{8a10} OH	32.4 ± 4.57	1527 ± 71	5.0 ± 1.3	12.5
PEU _{8a15} A	HOPCL _{8a15} OH	26.1 ± 4.13	1641 ± 144	3.1 ± 0.6	20.0
PEU _{12a5} A	HOPCL _{12a5} OH	22.4 ± 3.35	774 ± 99	87.9 ± 13.4	9.0
PEU _{12a10} A	HOPCL _{12a10} OH	30.9 ± 6.62	1482 ± 168	5.1 ± 2.8	12.0
PEU _{12a15} A	HOPCL _{12a15} OH	19.6 ± 2.37	1198 ± 235	108.0 ± 2.0	19.0
PEU _{4a5} B	HOPCL _{4a5} OH	24.4 ± 3.85	1193 ± 96	4.1 ± 1.0	-
PEU _{4a10} B	HOPCL _{4a10} OH	19.3 ± 2.10	1747 ± 81	2.9 ± 0.5	-
PEU _{4a15} B	HOPCL _{4a15} OH	30.6 ± 4.85	1684 ± 144	63.8 ± 6.2	18.0
PEU _{8a5} B	HOPCL _{8a5} OH	16.8 ± 2.51	1177 ± 39	4.4 ± 1.5	-
PEU _{8a10} B	HOPCL _{8a10} OH	19.3 ± 3.50	1705 ± 134	4.3 ± 0.8	-
PEU _{8a15} B	HOPCL _{8a15} OH	22.1 ± 2.41	1201 ± 71	13.1 ± 10.7	8.0
PEU _{12a5} B	HOPCL _{12a5} OH	13.9 ± 2.29	1088 ± 55	3.9 ± 1.1	-
PEU _{12a10} B	HOPCL _{12a10} OH	19.3 ± 1.37	1670 ± 92	11.5 ± 18.5	1.0
PEU _{12a15} B	HOPCL _{12a15} OH	29.2 ± 4.1	1552 ± 61	43.9 ± 22.7	16.0
PEU _{4a5} C	HOPCL _{4a5} OH	22.7 ± 2.98	1678 ± 48	5.6 ± 1.8	-
PEU _{4a10} C	HOPCL _{4a10} OH	9.2 ± 1.17	1778 ± 155	1.4 ± 0.2	-
PEU _{4a15} C	HOPCL _{4a15} OH	14.4 ± 1.31	865 ± 32	95.6 ± 11.1	15.0
PEU _{8a5} C	HOPCL _{8a5} OH	11.2 ± 3.60	2023 ± 95	2.8 ± 1.0	1.0
PEU _{8a10} C	HOPCL _{8a10} OH	9.3 ± 1.48	2931 ± 229	1.3 ± 0.3	-
PEU _{8a15} C	HOPCL _{8a15} OH	39.6 ± 3.16	1710 ± 65	5.0 ± 0.6	4.0
PEU _{12a5} C	HOPCL _{12a5} OH	21.0 ± 3.53	1424 ± 61	8.4 ± 2.5	-
PEU _{12a10} C	HOPCL _{12a10} OH	13.8 ± 4.40	1571 ± 78	3.1 ± 1.2	1.0
PEU _{12a15} C	HOPCL _{12a15} OH	20.2 ± 2.23	1442 ± 211	42.5 ± 3.8	18.0

HOPCLOH, α,ω -hydroxy telechelic poly(ϵ -caprolactone); PCL, poly(ϵ -caprolactone); PEU, poly(ester-urethane); A, 1,6-hexamethylene diisocyanate (HDI); B, methylene diphenyl diisocyanate (MDI); C, 4,4'-methylenebis (cyclohexyl isocyanate) (HMDI). DSC, differential scanning calorimetry.

^aHOPCLOH= HO – PCL – OH or HO – (CH₂)_m – PCL – OH, where m = 4, 8, and 12.

^bObtained by DSC.

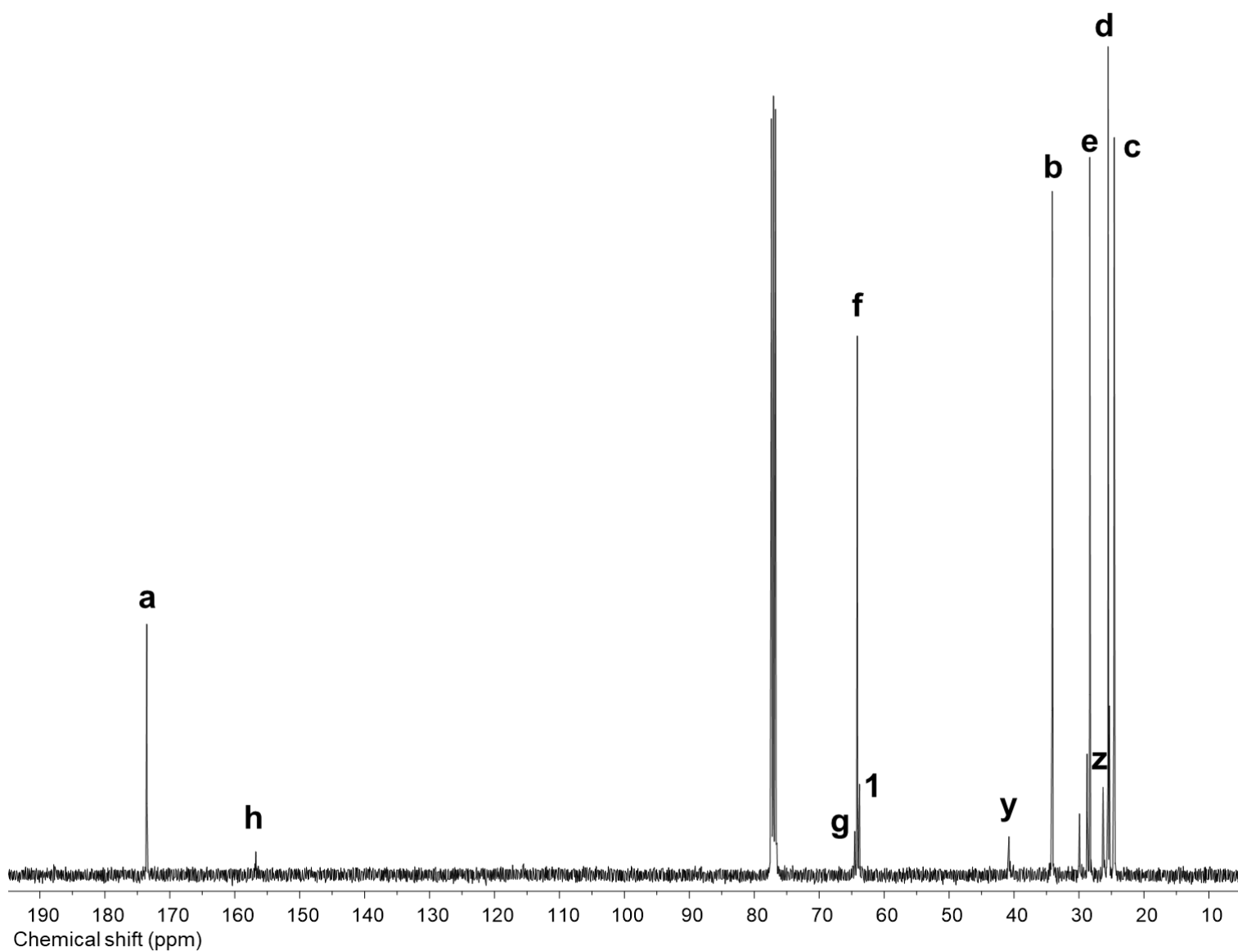
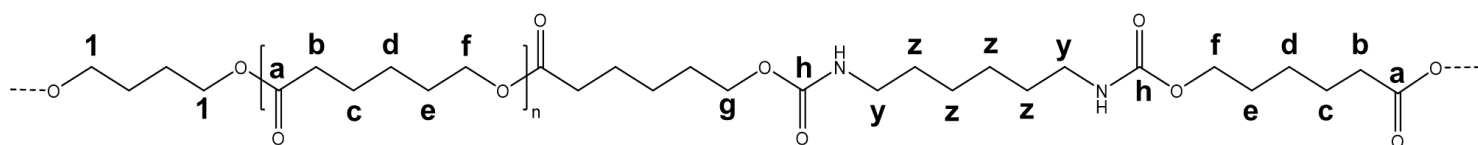


Fig. S1. ¹³C NMR (100 MHz) spectrum in CDCl₃ at room temperature for PEU_{4a10A}.

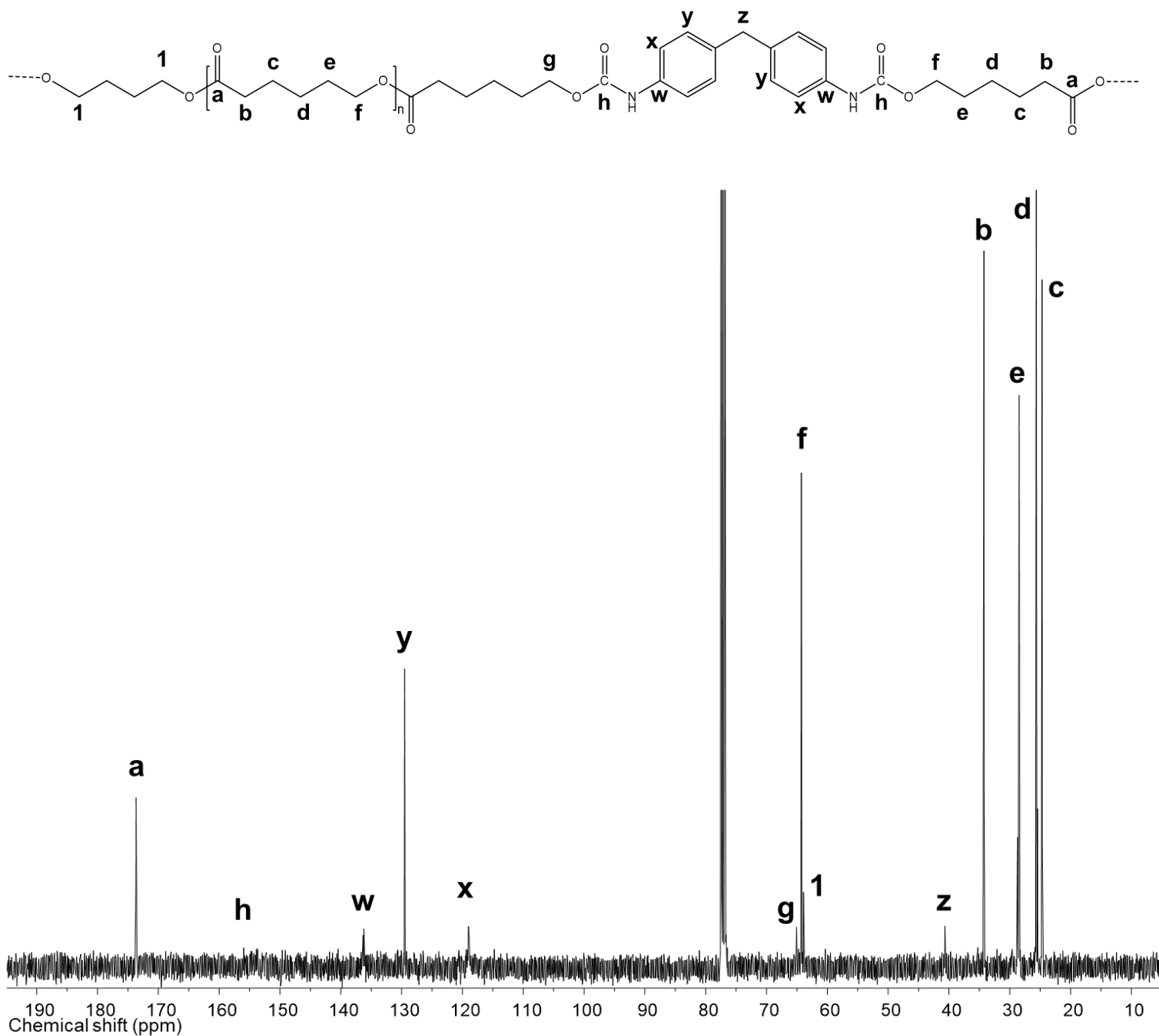


Fig. S2. ¹³C NMR (100 MHz) spectrum in CDCl₃ at room temperature for PEU_{4a10B}.

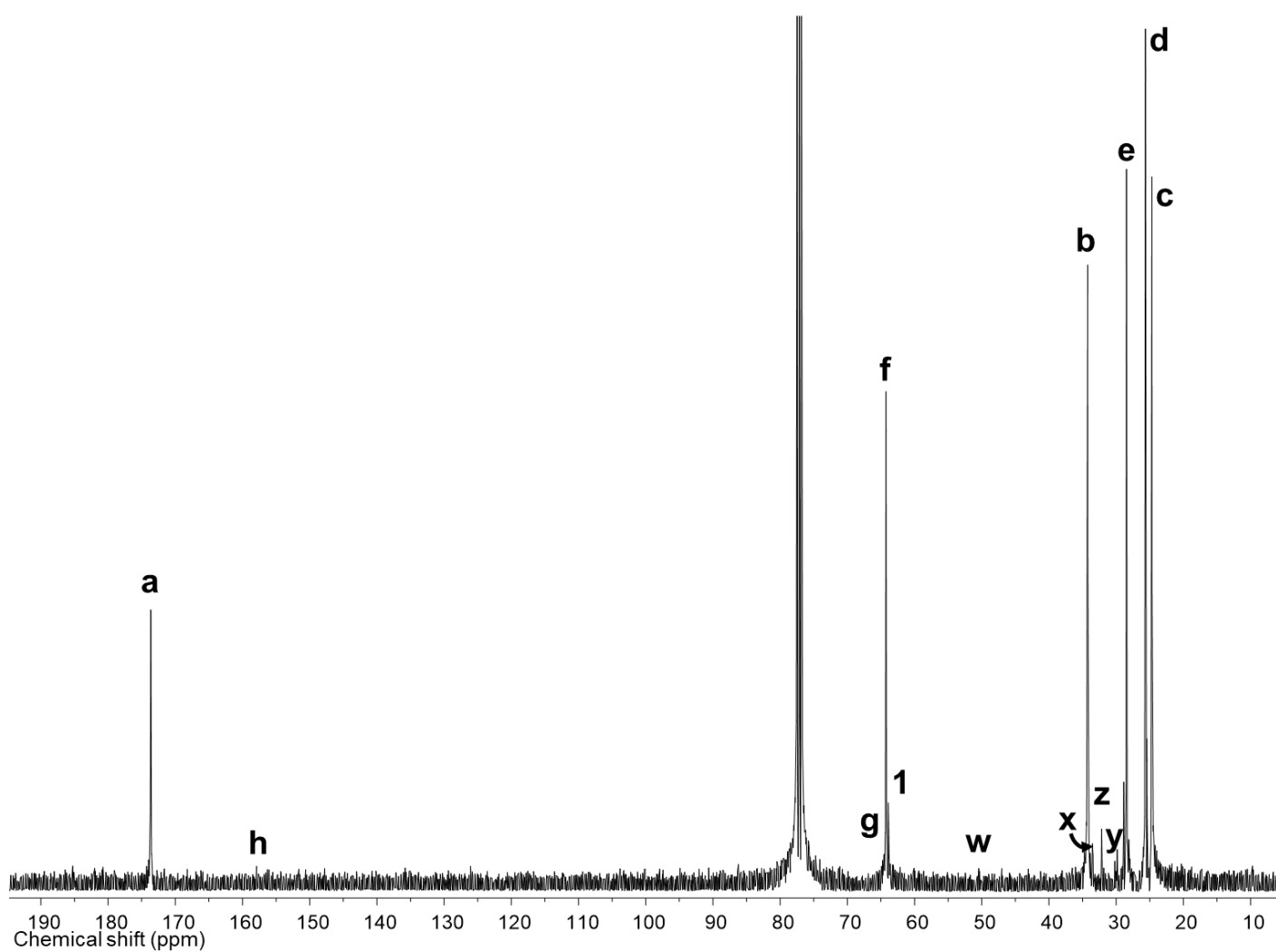
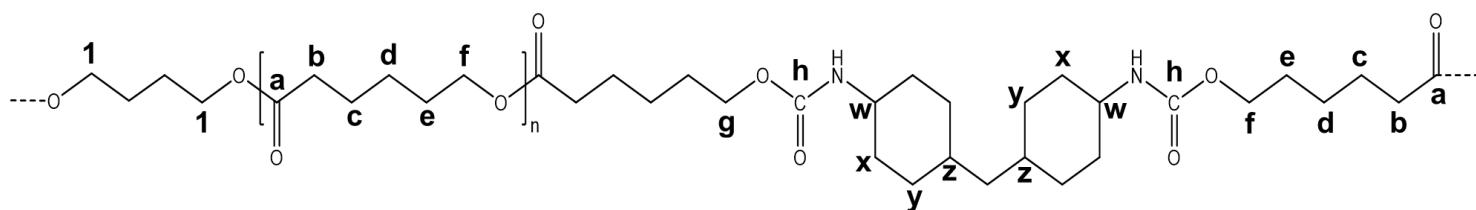


Fig. S3. ^{13}C NMR (100 MHz) spectrum in CDCl_3 at room temperature for PEU_{4a10C} .

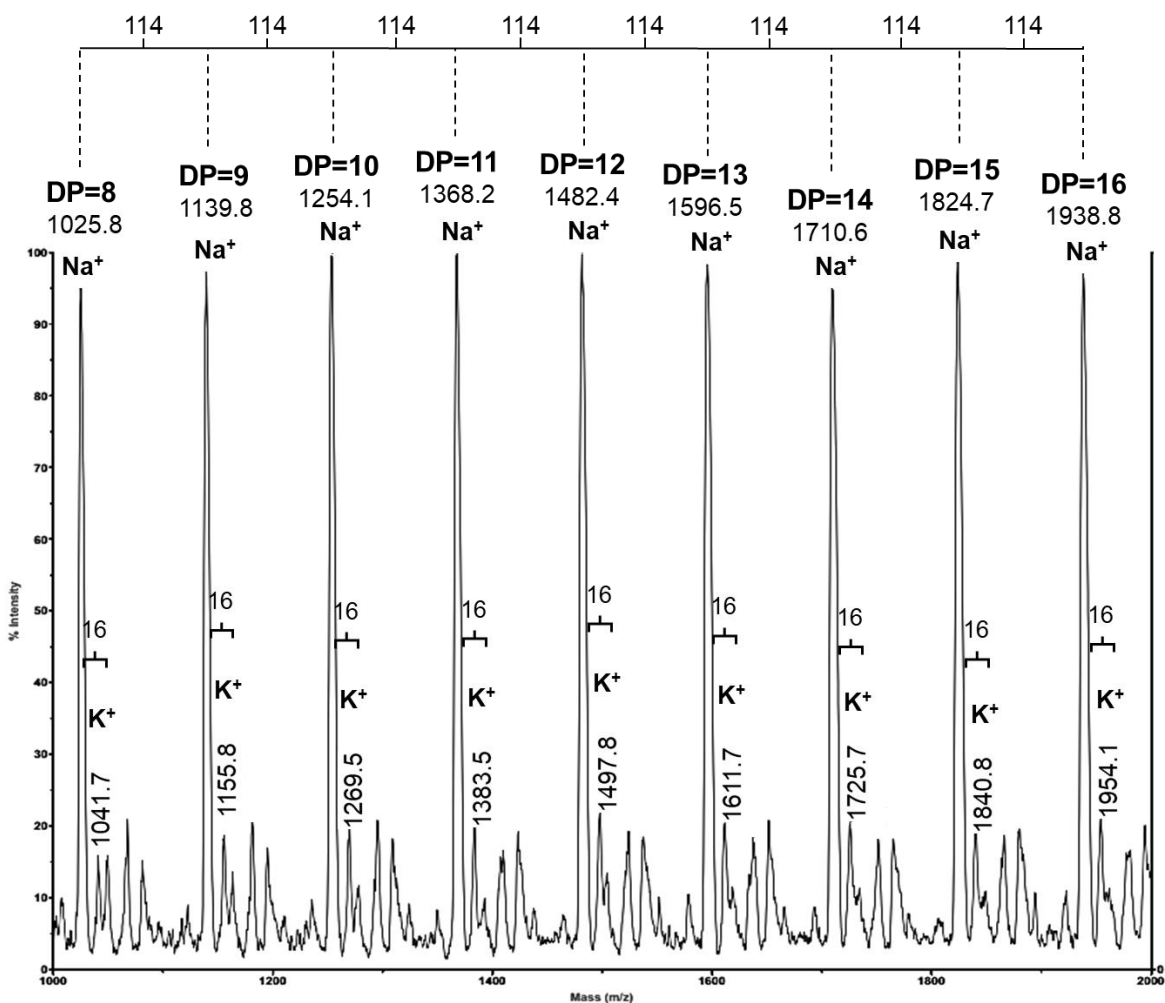


Fig. S4. MALDI-TOF spectrum (linear mode) expanded view for the 1000–2000 m/z fragments of HOPCL_{4a10}OH (note: 114 and 16 are the values of the molecular weight of CL and the difference between Na⁺ and K⁺ (doping the same species of polymer), respectively).

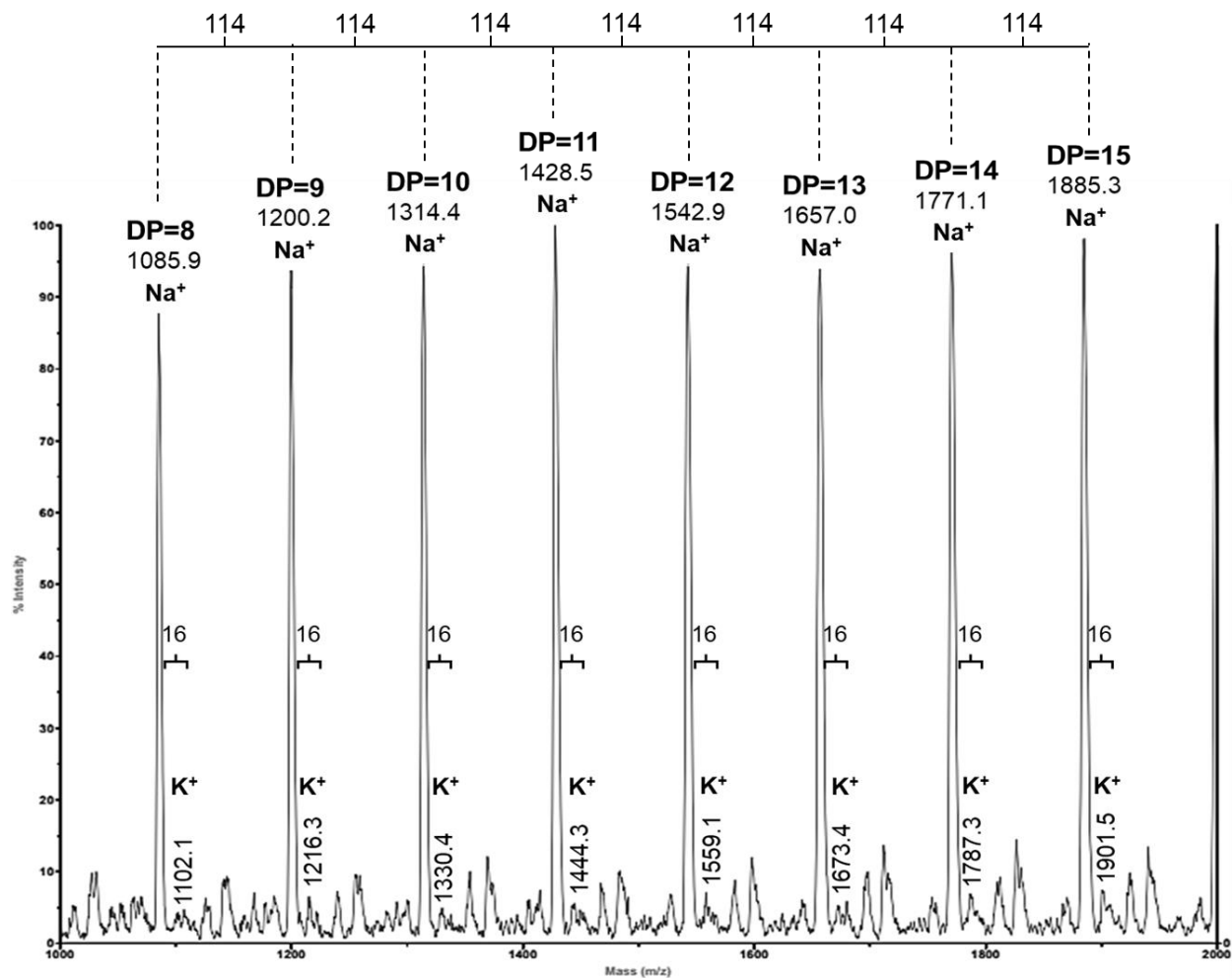


Fig. S5. MALDI-TOF spectrum (linear mode) expanded view for the 1000–2000 m/z fragments of HOPCL_{8a10}OH (note: 114 and 16 are the values of the molecular weight of CL and the difference between Na⁺ and K⁺ (doping the same species of polymer), respectively).

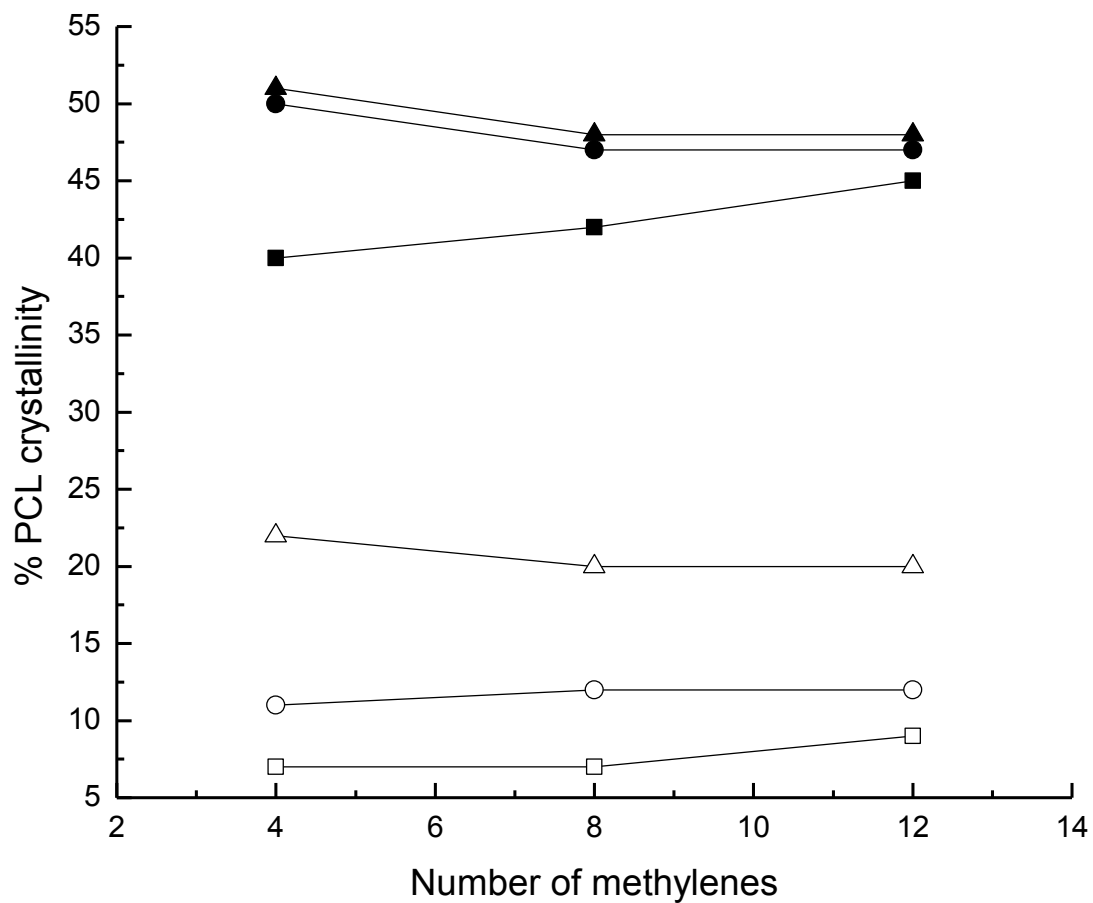


Fig. S6. Effect of number of methylenes on the crystallinity PCL for poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and 1,6-hexamethylene diisocyanate (HDI). The PEUs derived from the macrodiols with DP=5 as initiator are indicated with open squares \square , and macrodiols are indicated with filled square \blacksquare ; PEUs derived from macrodiols with DP=10 as initiator are indicated with open circles \circ , and macrodiols are indicated with filled circles \bullet , and PEUs derived from macrodiols with DP=15 as initiator are indicated with open triangles \triangle , and macrodiols are indicated with filled triangle \blacktriangle .

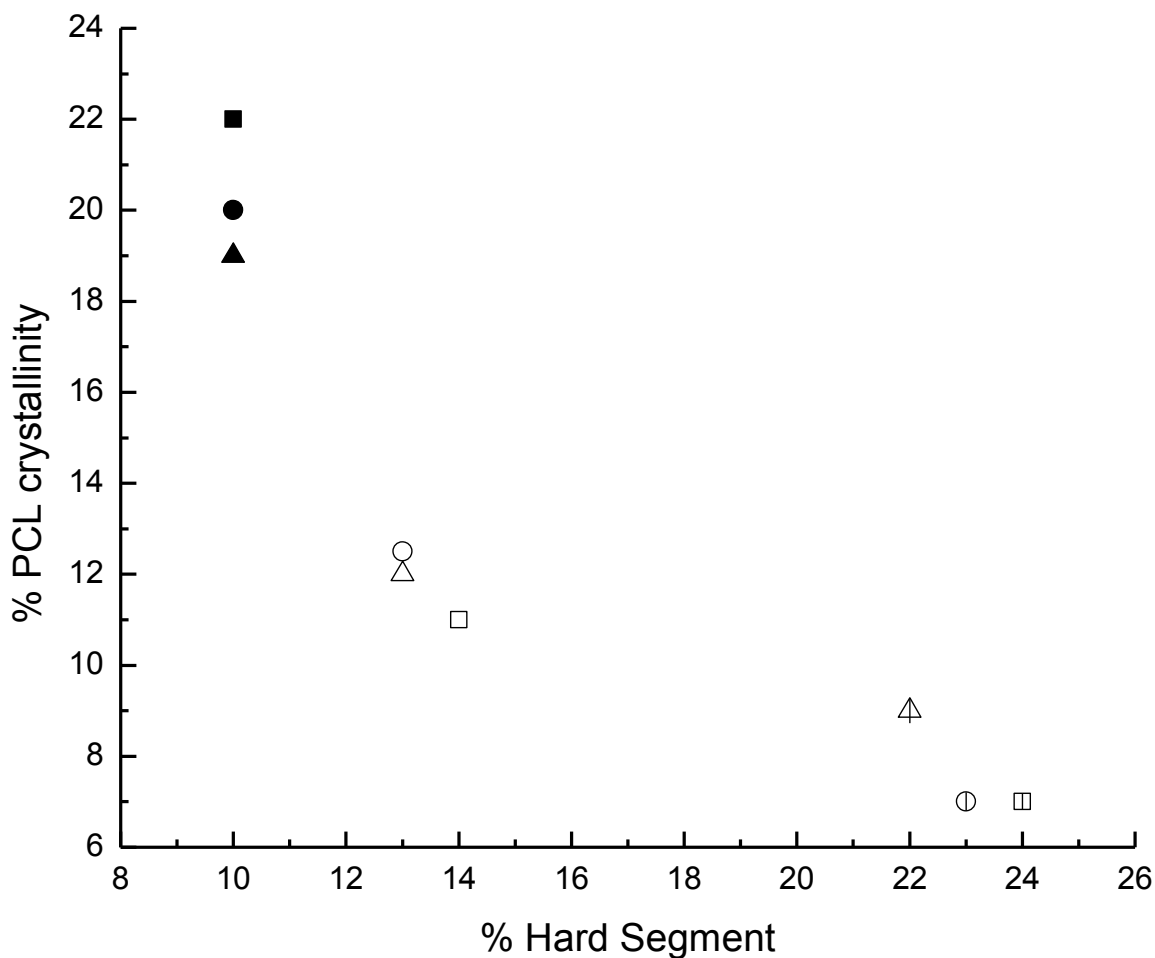


Fig. S7. Effect of Hard Segment (HS) content on the crystallinity PCL for poly(ester-urethanes) (PEUs) derived from poly(ϵ -caprolactone) diols (HOPCLOH) and 1,6-hexamethylene diisocyanate (HDI). The PEUs derived from the macrodiols with HO(CH₂)₄OH as initiator are indicated with squares (\square DP=5; \square DP=10, and \blacksquare DP=15); PEUs derived from macrodiols with HO(CH₂)₈OH as initiator are indicated with circles (\odot DP=5, \circ DP=10, and \bullet DP=15) and PEUs derived from macrodiols with HO(CH₂)₁₂OH as initiator are indicated with triangles (\triangle DP=5, \triangle DP=10, and \blacktriangle DP=15).

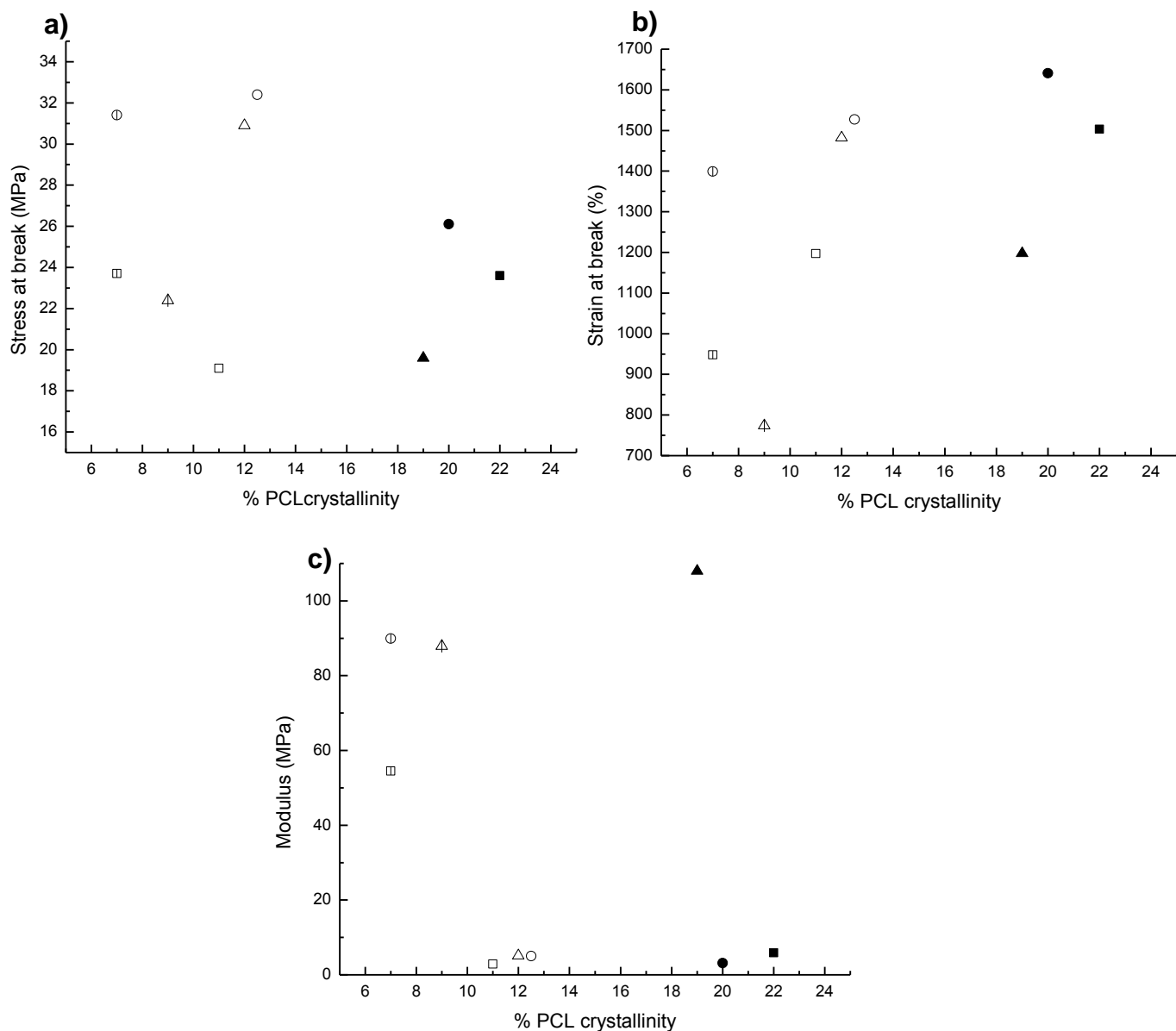


Fig. S8. Mechanical properties of the synthesized PEUs with HDI: a) stress at break, b) strain at break, and c) modulus. The PEUs derived from the macrodiols with HO(CH₂)₄OH as initiator are indicated with squares (◻ DP=5, ◻ DP=10, and ◼ DP=15); PEUs derived from macrodiols with HO(CH₂)₈OH used as initiator are indicated with circles (⊕ DP=5, ○ DP=10, and ● DP=15) and PEUs derived from macrodiols with HO(CH₂)₁₂OH as initiator are indicated with triangles (△ DP=5, △ DP=10, and ▲ DP=15).