

## Supporting Information

for

### **Influence of the hard segments content on the properties of electrospun aliphatic poly(carbonate-urethane-urea)s**

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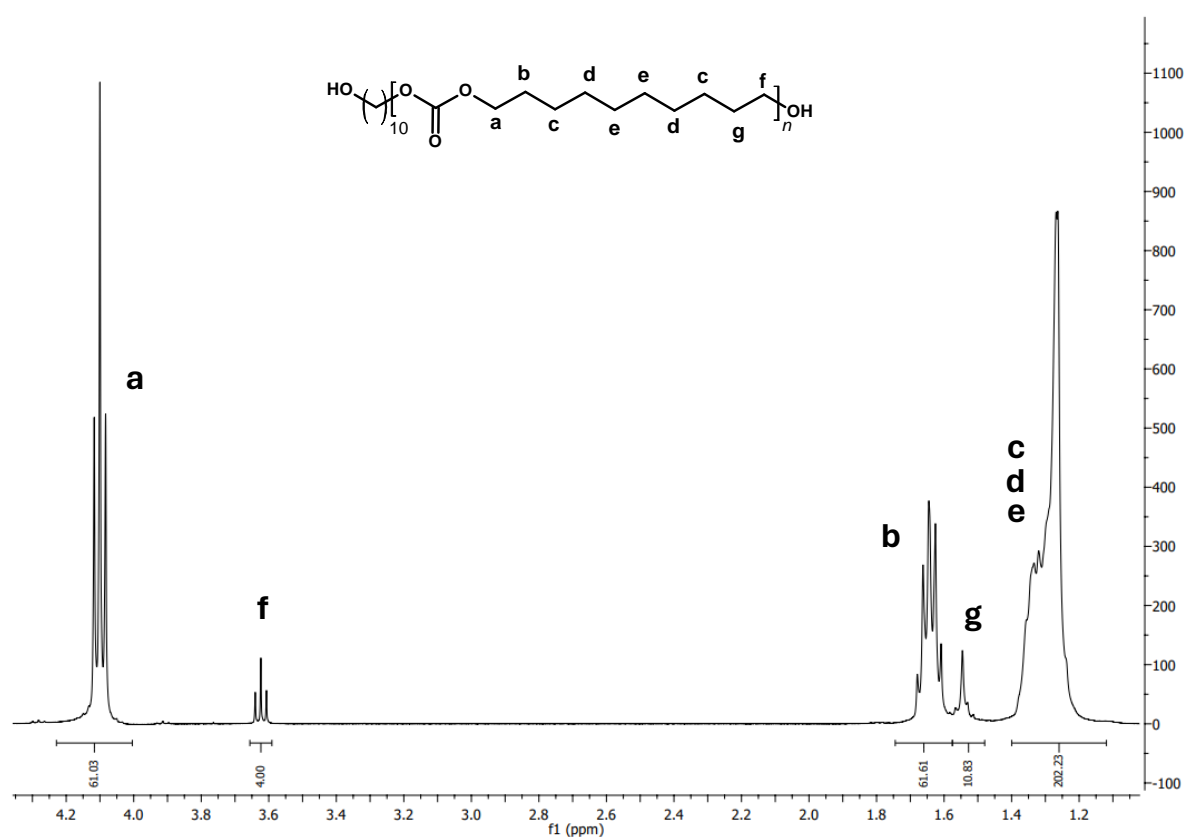
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## Procedure of the synthesis of oligo(decamethylene carbonate) diol (OCD)

The 56.5 g of 1,10-decanediol (0.32 mol), 150.0 g of E\_BMC\_8 (0.52 mol) and K<sub>2</sub>CO<sub>3</sub> (0.005 mol.%) were placed in a 500 cm<sup>3</sup> three-necked flask equipped with a magnetic stirrer, thermometer, and distillation condenser. Then, approximately 60 cm<sup>3</sup> of 1,4-dioxane was added. The temperature of the mixture was gradually increased from 100 °C to 160 °C. The progress of the reaction was monitored by measuring the refractive index of the distillate and carried out until no methanol was observed in the distillate (around 14 h). Afterwards, the reaction was continued under reduced pressure at 160 °C (for an additional 4 h), while the 1,10-decanediol and residual 1,4-dioxane were removed. The obtained product was dissolved in dichloromethane and washed six times with demineralized water to remove the catalyst. Afterwards, the solvent and residuals of water were removed under reduced pressure. The synthesized product was characterized by <sup>1</sup>H NMR and FTIR spectroscopy. Based on <sup>1</sup>H NMR, the number average molar mass was calculated to be equal 3000 g·mol<sup>-1</sup>.

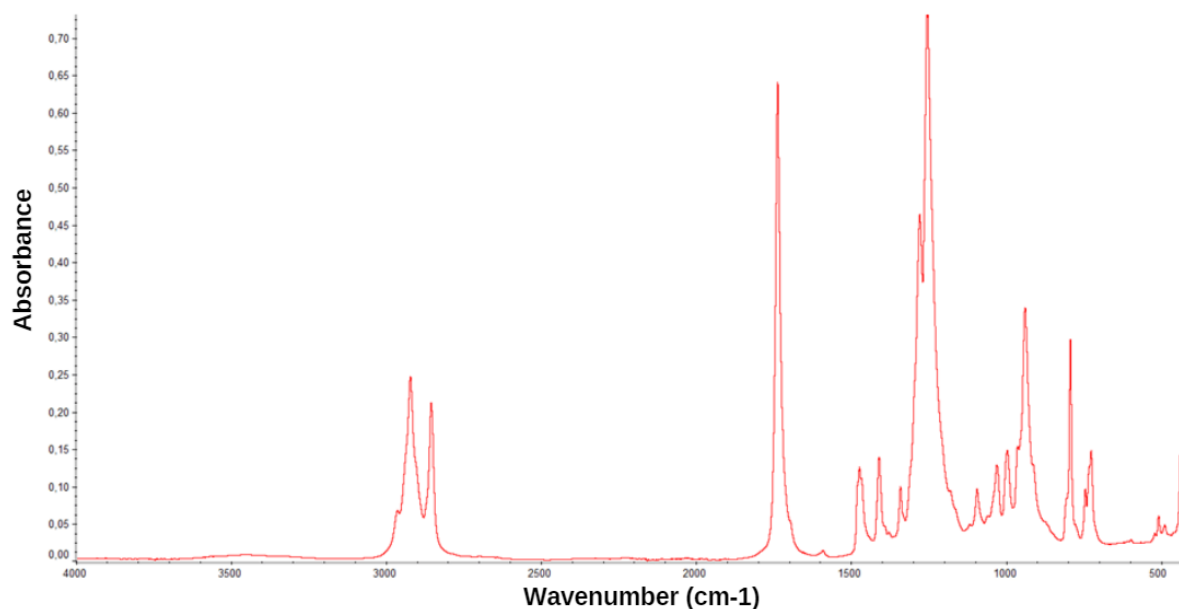
OCD:



**Figure S1.** <sup>1</sup>H NMR spectrum of OCD.

<sup>1</sup>H NMR: (CDCl<sub>3</sub>, 400MHz): δ (ppm)= 4.10 (t, 4H, C(O)OCH<sub>2</sub>), 3.62 (t, 4H, CH<sub>2</sub>OH), 1.65

(m, 4H, HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.55 (m, 4H, HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.53 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.32 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.27 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).



**Figure S2.** FTIR (ATR) spectrum of OCD.

FTIR (ATR): 3450, 2920, 2850, 1740, 1470, 1400, 1340, 1280, 1250, 1030, 940, 790  $\text{cm}^{-1}$ .

Specimens were named accordingly: **PCUU\_X** where **X** means the molar excess of the IPDI used for the synthesis. For example, **PCUU\_1.5** means that the film was obtained from OCD and IPDI in the molar ratio of 1:1.5

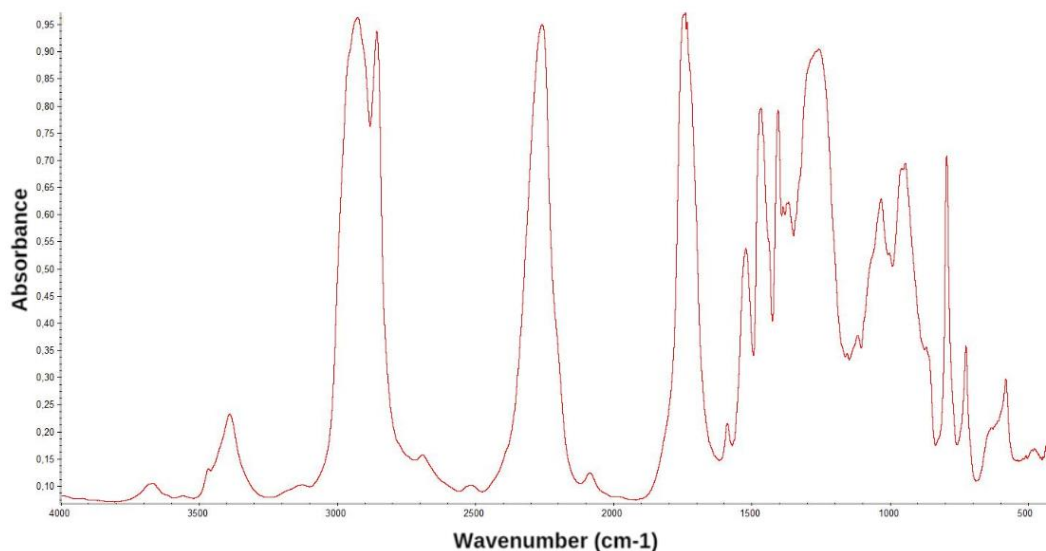
**Table S1.** The amount of reagents used in the syntheses of the PCUUs.

PCUU	N_3	N_2.5	N_2	N_1.5
OCD	20.00 g	20.00 g	20.02 g	20.00 g
IPDI	4.40 g	3.70 g	2.95 g	2.24 g

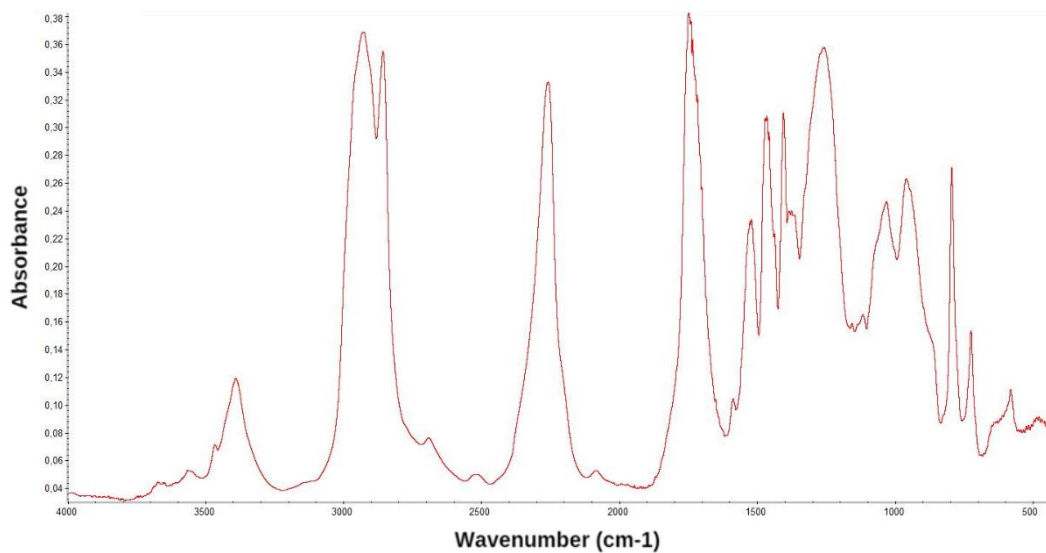
### FTIR analysis of prepolymers:

The region 3200-3800  $\text{cm}^{-1}$  is assigned to N-H stretching bands. The broad absorption bands 2800–3000  $\text{cm}^{-1}$  correspond to the stretching vibration of CH<sub>2</sub> groups. At 2260  $\text{cm}^{-1}$  is assigned to NCO stretching bands. In the range of 1620–1780  $\text{cm}^{-1}$  the bands of carbonyl groups are

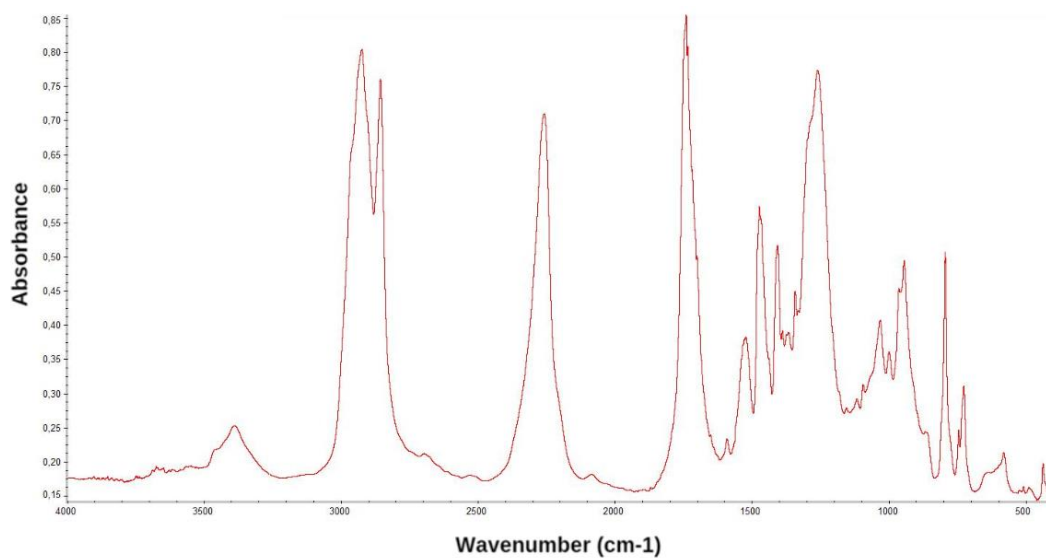
present representing the following groups: amide I (non-hydrogen bonded urethane around  $1700\text{ cm}^{-1}$  and hydrogen-bonded urethane around  $1690\text{ cm}^{-1}$ ), carbonate (hydrogen-bonded around  $1720\text{ cm}^{-1}$  and non-hydrogen bonded around  $1740\text{ cm}^{-1}$ ). Amide II bands from urethane could also be identified in the spectra and located around  $1520\text{-}1565\text{ cm}^{-1}$ .



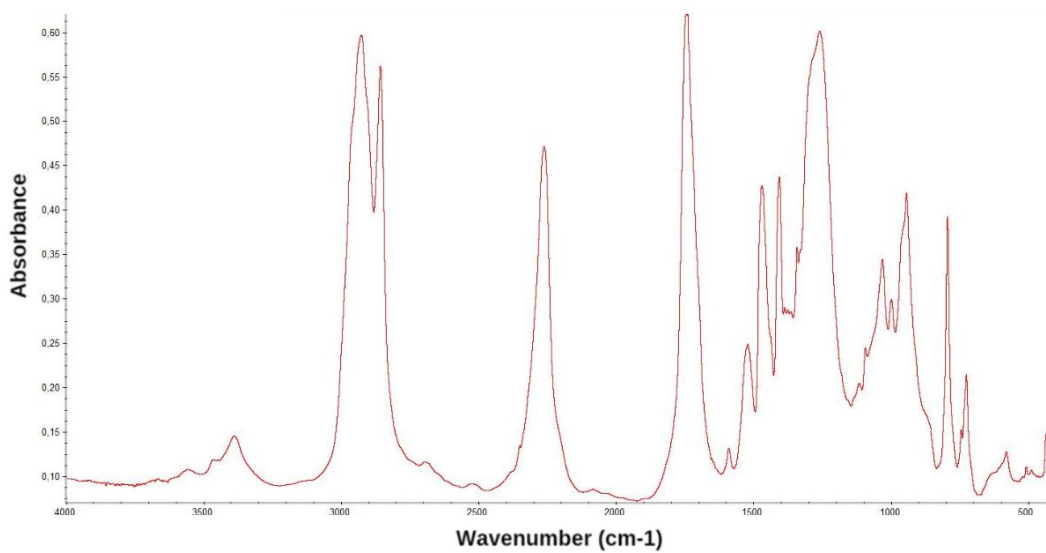
**Figure S3.** FTIR spectra of PCUU\_3 carbonate-urethane diisocyanate prepolymer.



**Figure S4.** FTIR spectra of PCUU\_2.5 carbonate-urethane diisocyanate prepolymer.



**Figure S5.** FTIR spectra of PCUU\_2 carbonate-urethane diisocyanate prepolymer.



**Figure S6.** FTIR spectra of PCUU\_1.5 carbonate-urethane diisocyanate prepolymer.

PCUU\_3.0

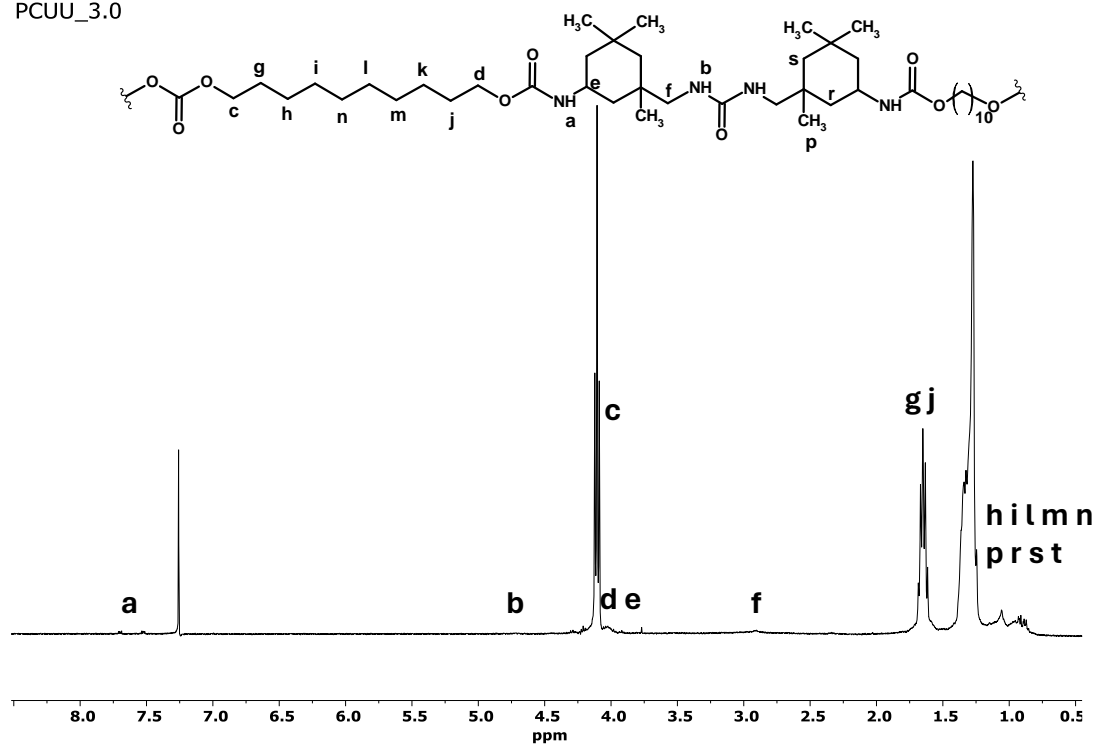


Figure S7. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) spectrum of PCUU\_3.

PCUU\_2.5

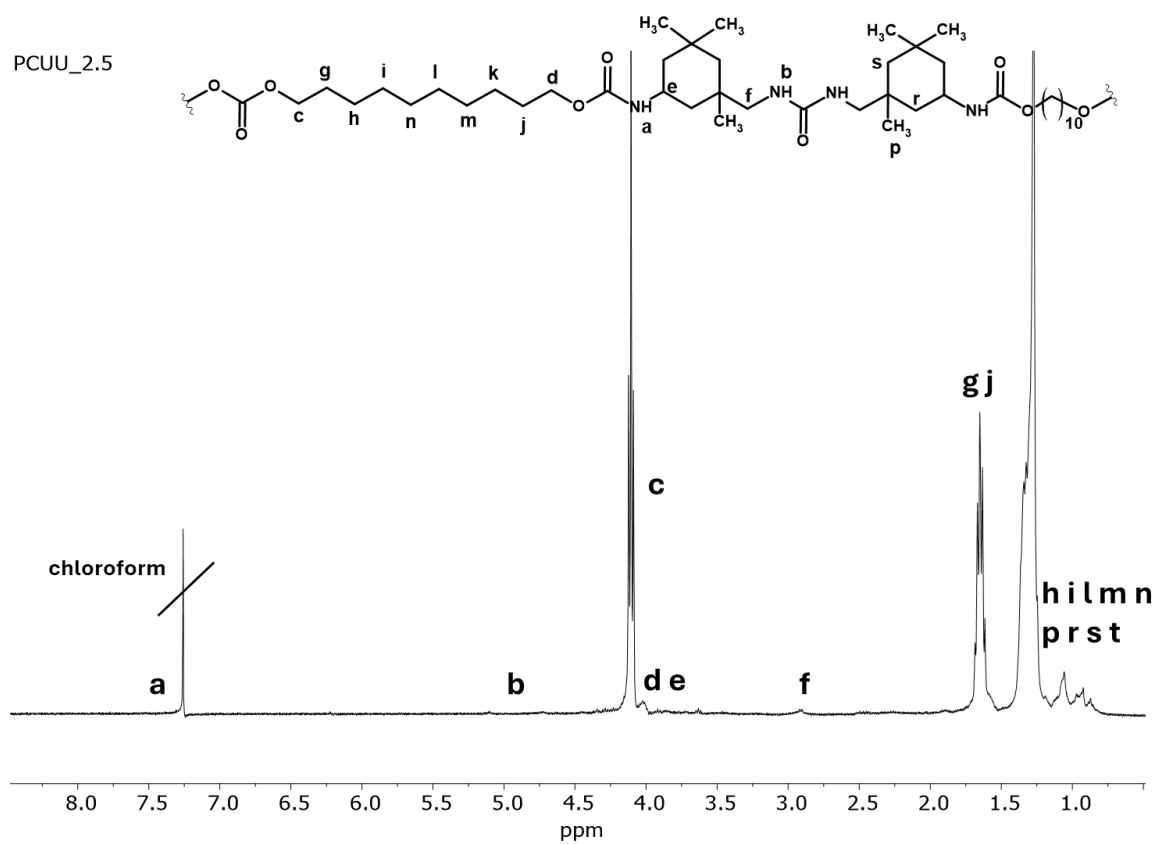
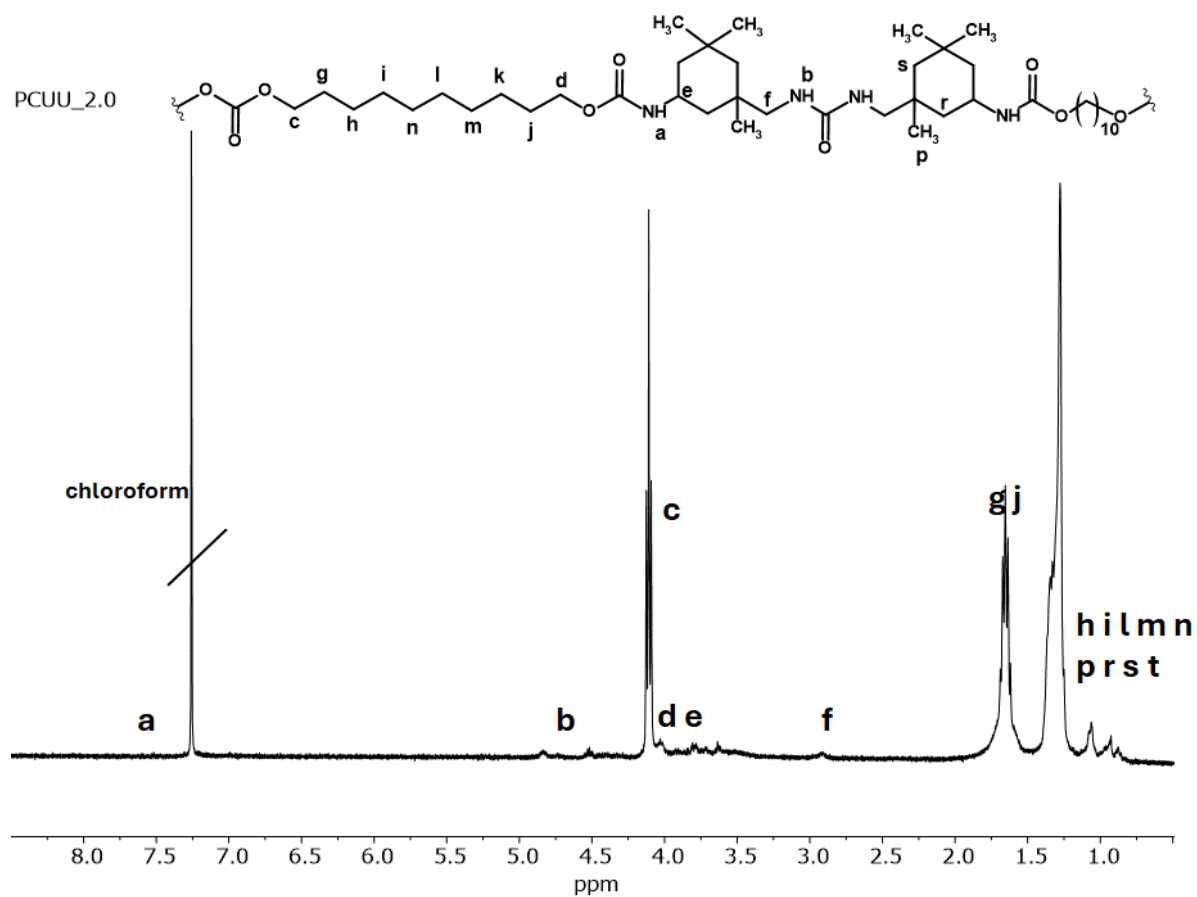
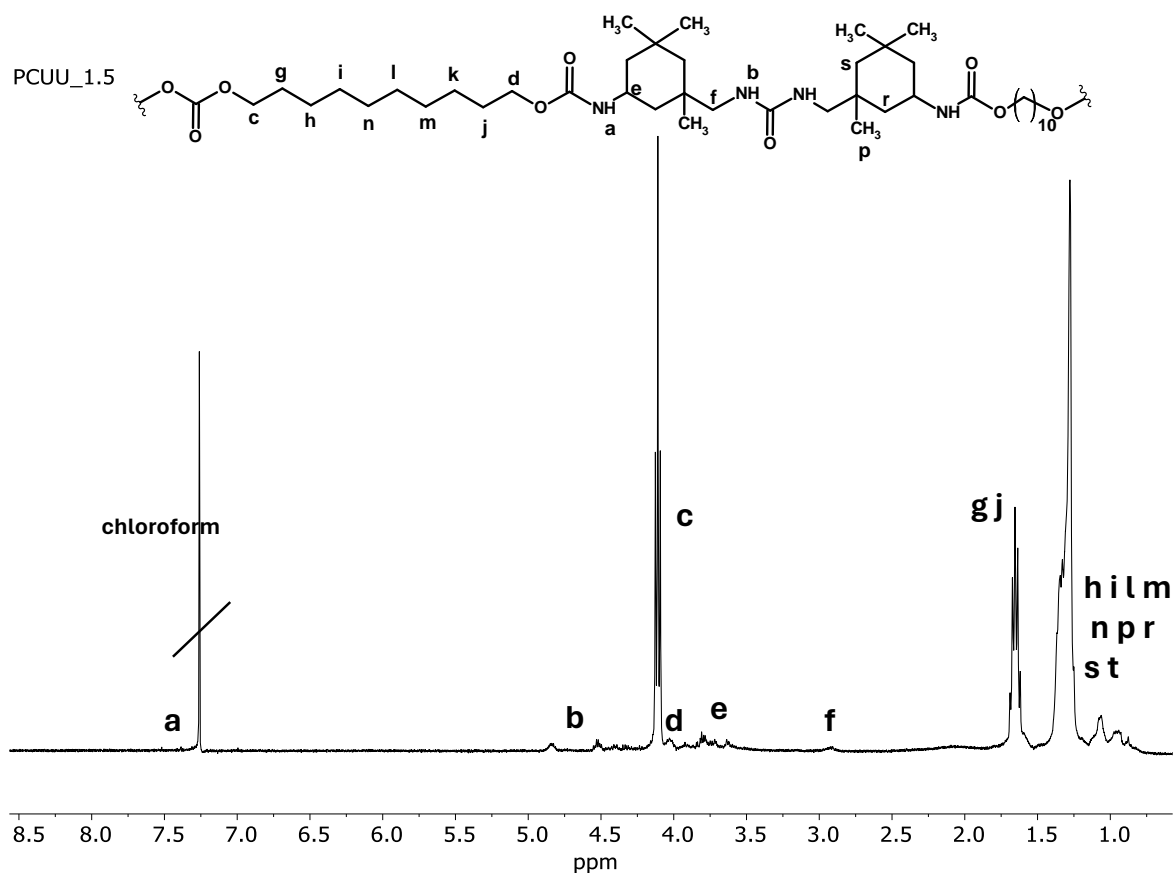


Figure S8. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz) spectrum of PCUU\_2.5.



**Figure S9.**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz) spectrum of PCUU\_2.

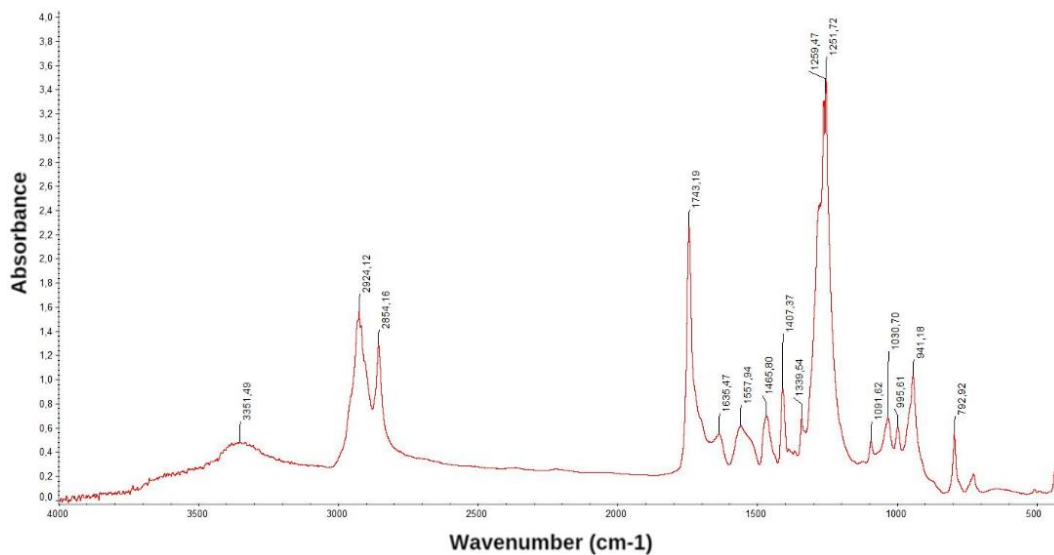


**Figure S10.**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz) spectrum of PCUU\_1.5.

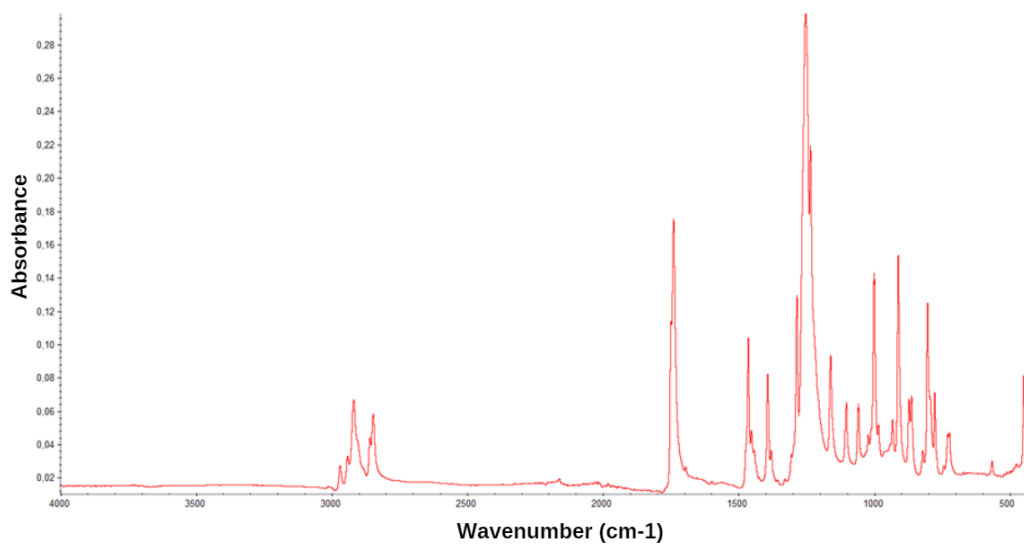
**FTIR analysis:**

The region  $3200\text{--}3500\text{ cm}^{-1}$  is assigned to N-H stretching bands. The broad absorption bands  $2800\text{--}3000\text{ cm}^{-1}$  correspond to the stretching vibration of  $\text{CH}_2$  groups. In the range of  $1620\text{--}1780\text{ cm}^{-1}$  the bands of carbonyl groups are present representing the following groups: amide I (non-hydrogen bonded urethane around  $1700\text{ cm}^{-1}$  and hydrogen-bonded urethane around  $1690\text{ cm}^{-1}$ ), carbonate (hydrogen-bonded around  $1720\text{ cm}^{-1}$  and non-hydrogen bonded around  $1740\text{ cm}^{-1}$ ), and hydrogen-bonded urea carbonyl band at nearly  $1630\text{ cm}^{-1}$ . Amide II bands from urethane and urea could also be identified in the spectra and located around  $1520\text{--}1565\text{ cm}^{-1}$ .

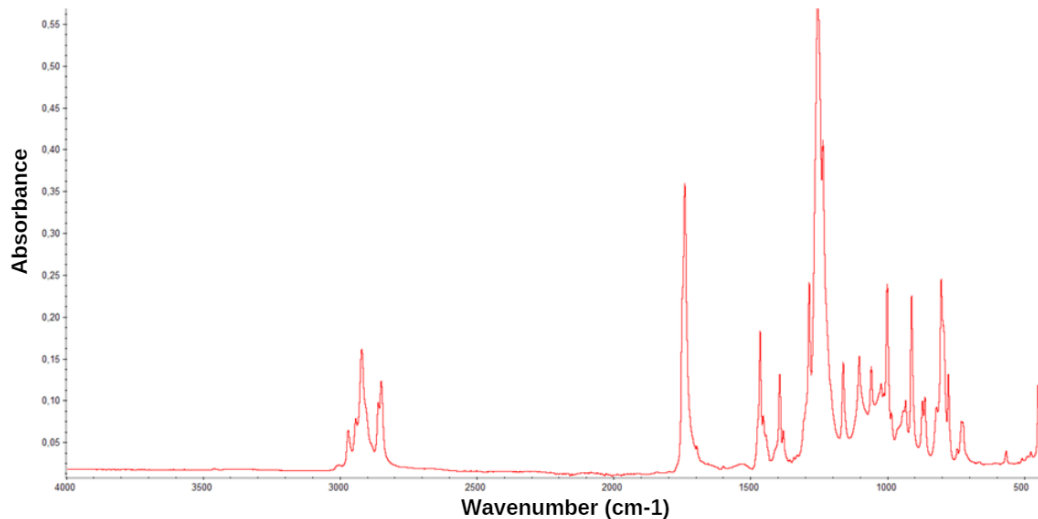




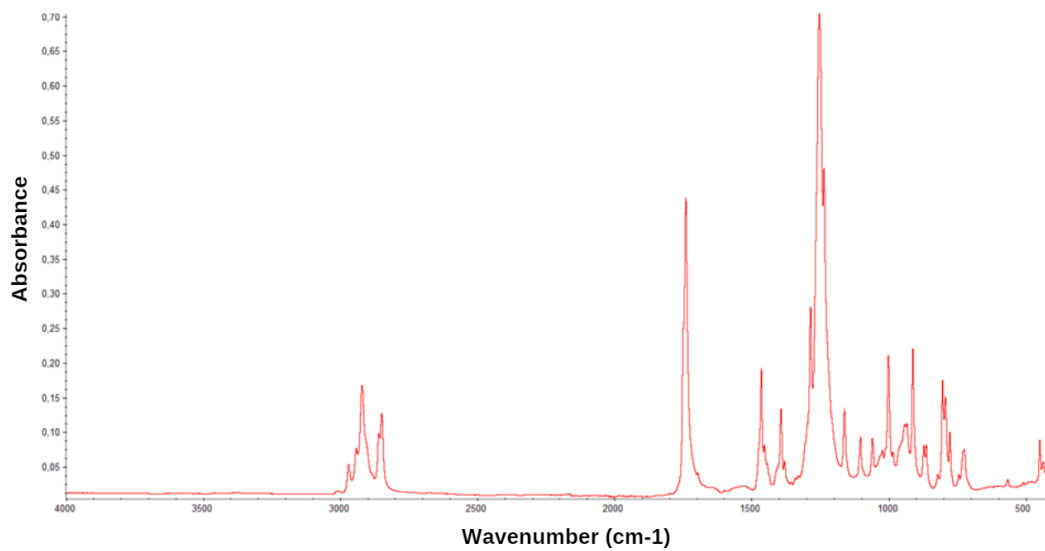
**Figure S11.** FTIR spectra of PCUU\_3.



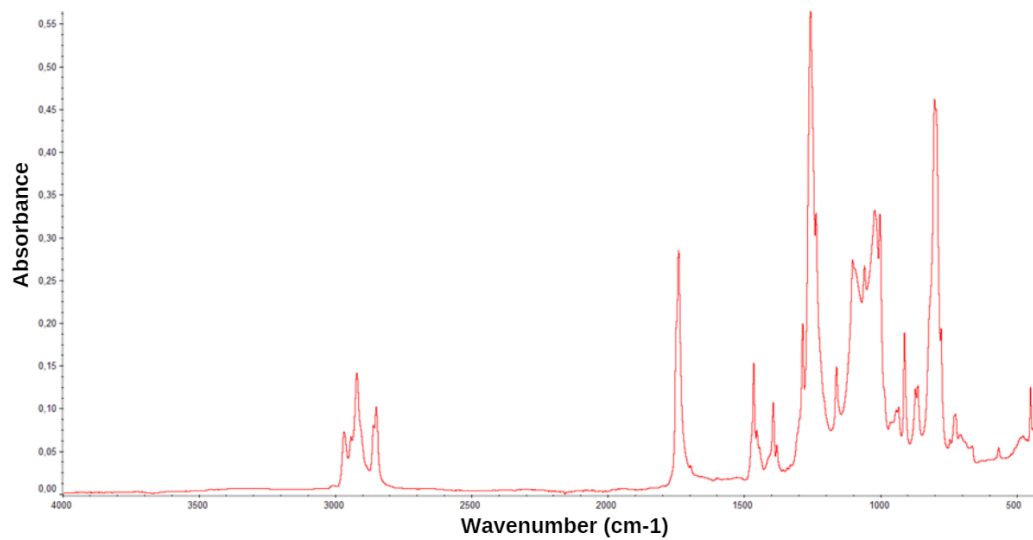
**Figure S12.** ATR-FTIR spectrum of PCUU\_3.



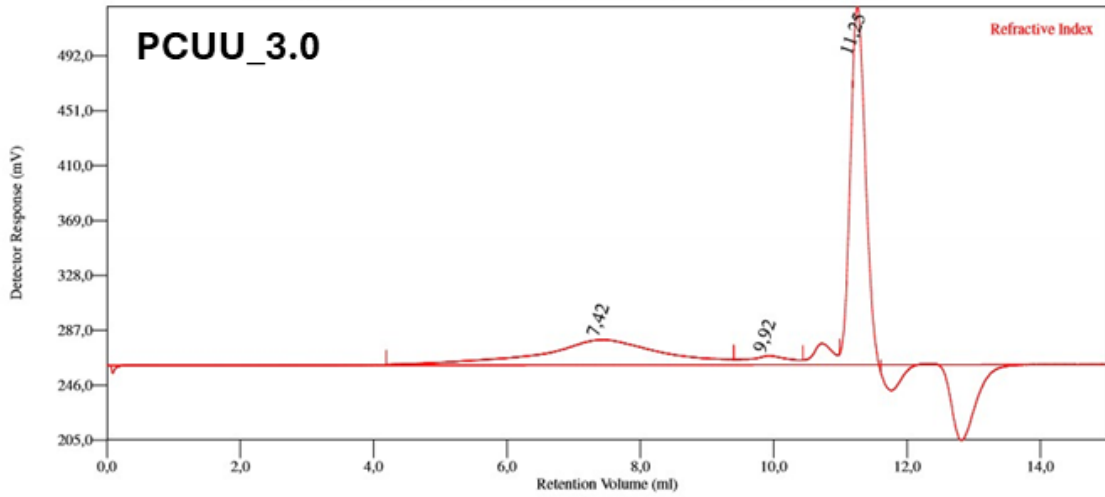
**Figure S13** ATR-. FTIR spectrum of PCUU\_2.5.



**Figure S14.** ATR-FTIR spectrum of PCUU\_2.



**Figure S15** ATR-FTIR spectrum of PCUU\_1.5.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	7.423	9.923	11.247
Mn - (Daltons)	23 546	412	0
Mw - (Daltons)	2,008 e 6	685	0
Mz - (Daltons)	1,046 e 8	1 005	0
Mp - (Daltons)	62 675	537	0
Mw / Mn	85,298	1,663	0,000
Percent Above Mw:	0	100,000	0,000
Percent Below Mw:	0	0,000	0,000
Mw 10.0% Low	5 064	151	0
Mw 10.0% High	1,889 e 7	1 684	0
Wt Fr (Peak)	0,888	0,112	0,000
RI Area - (mVml)	39,94	5,04	69,82
UV@240nm Area - (mVml)	0,00	0,00	0,00

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Limits File	
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Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	120,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467

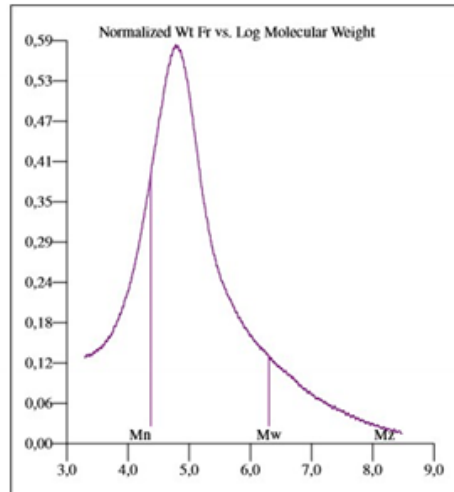
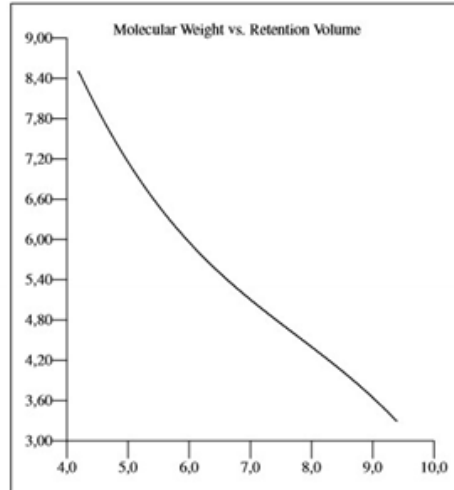
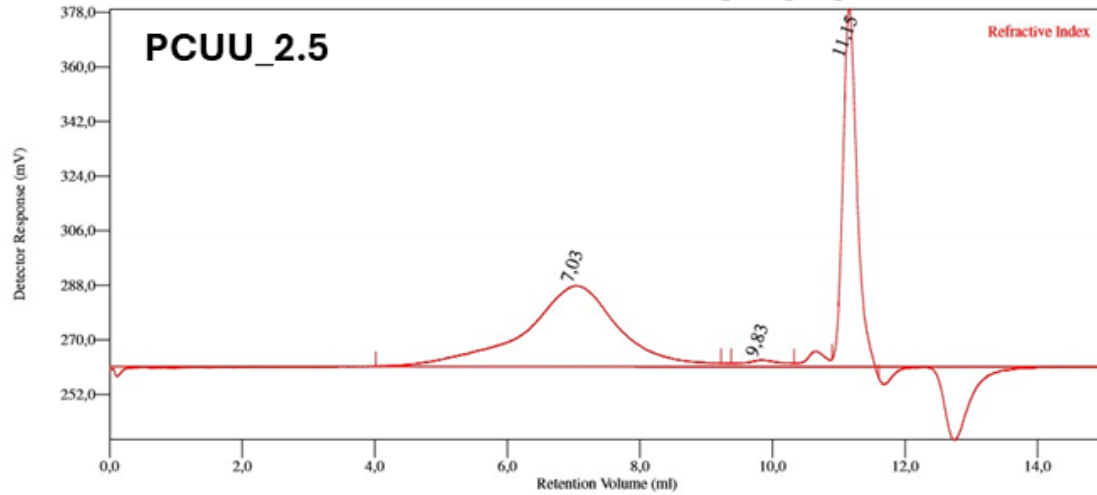


Figure S16. GPC curves of PCUU\_3.0.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	7,033	9,827	11,150
Mn - (Daltons)	56 286	406	0
Mw - (Daltons)	1,674 e 6	627	0
Mz - (Daltons)	1,338 e 8	881	0
Mp - (Daltons)	107 886	553	0
Mw / Mn	29,737	1,546	0,000
Percent Above Mw:	0	100,000	0,000
Percent Below Mw:	0	0,000	0,000
Mw 10.0% Low	15 608	157	0
Mw 10.0% High	1,415 e 7	1 468	0
Wt Fr (Peak)	0,968	0,032	0,000
RI Area - (mvm)	43,51	1,43	28,77
UV@240nm Area - (mvm)	0,00	0,00	0,00

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System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	50,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467

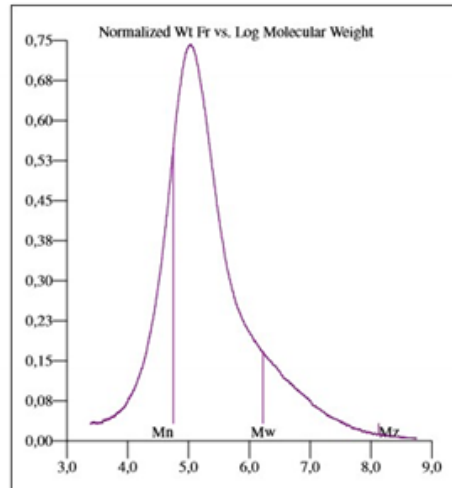
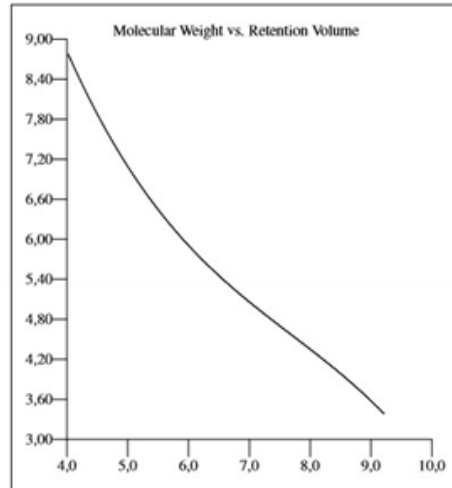
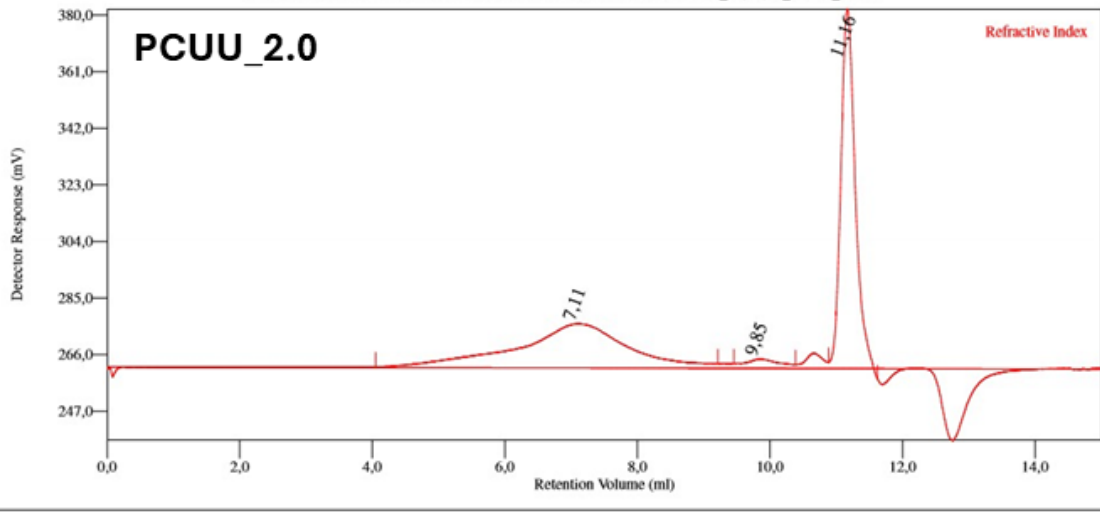


Figure S17. GPC curves of PCUU\_2.5.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	7,107	9,850	11,160
Mn - (Daltons)	43 746	366	0
Mw - (Daltons)	2,665 e 6	556	0
Mz - (Daltons)	1,303 e 8	759	0
Mp - (Daltons)	96 554	535	0
Mw / Mn	60 921	1 520	0 000
Percent Above Mw:	0	100 000	100 000
Percent Below Mw:	0	0 000	0 000
Mw 10.0% Low	10 586	138	0
Mw 10.0% High	2 427 e 7	1 250	0
Wt Fr (Peak)	0,937	0,063	0,000
RI Area - (mVml)	28,71	1,95	30,10
UV@240nm Area - (mVml)	0,00	0,00	0,00

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Column Set	Jordi DVB Mixed Bed
System	QDA MB
Flow Rate - (ml/min)	1,000
Inj Volume - (ul)	50,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467

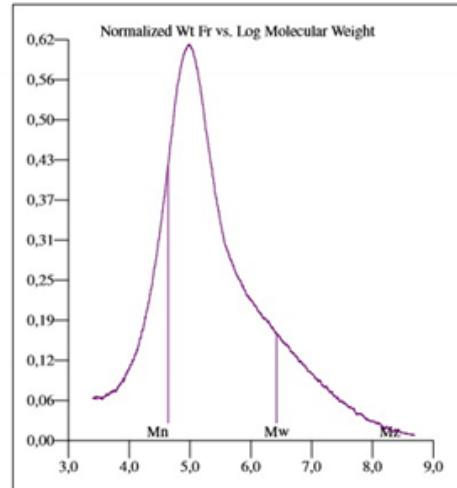
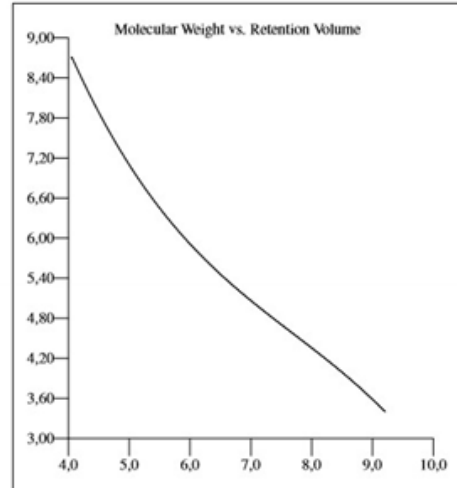
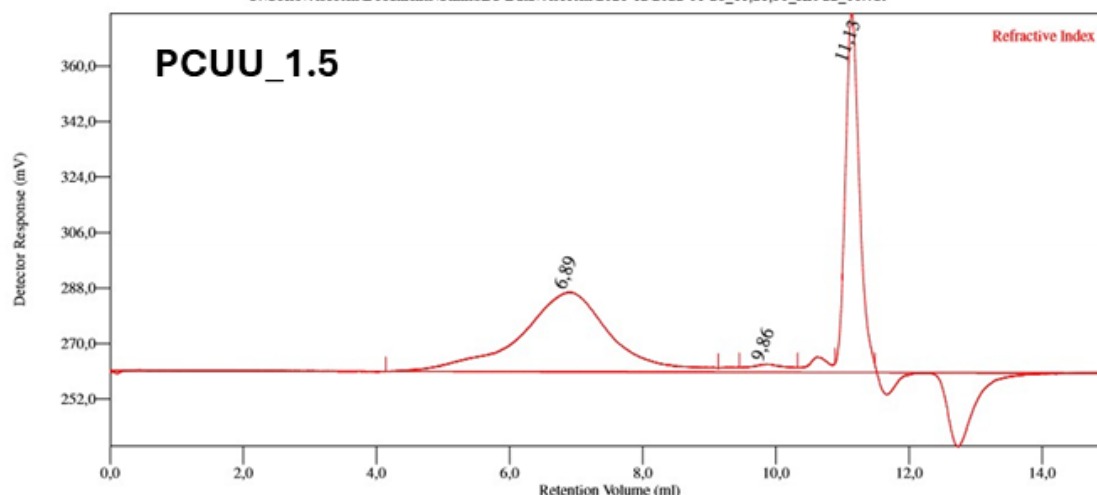


Figure S18. GPC curves of PCUU\_2.0.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	6,893	9,860	11,133
Mn - (Daltons)	64 588	363	0
Mw - (Daltons)	1,169 e 6	539	0
Mz - (Daltons)	5,951 e 7	733	0
Mp - (Daltons)	135 223	488	0
Mw / Mn	18,106	1,483	0,000
Percent Above Mw: 0	100,000	100,000	0,000
Percent Below Mw: 0	0,000	0,000	0,000
Mw 10.0% Low	18 087	147	0
Mw 10.0% High	8,029 e 6	1 206	0
Wt Fr (Peak)	0,959	0,041	0,000
RI Area - (mVml)	40,22	1,71	28,45
UV@240nm Area - (mVml)	0,00	0,00	0,00

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Inj Volume - (ul)	50,0
Volume Increment - (ml)	0,00333
Detector Temp. - (deg C)	30,0
Column Temp. - (deg C)	30,0
OmniSEC Build Number	467

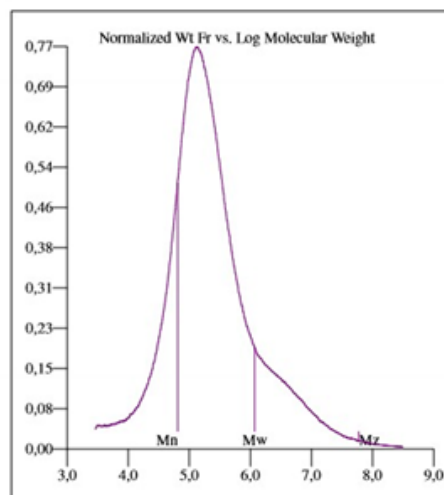
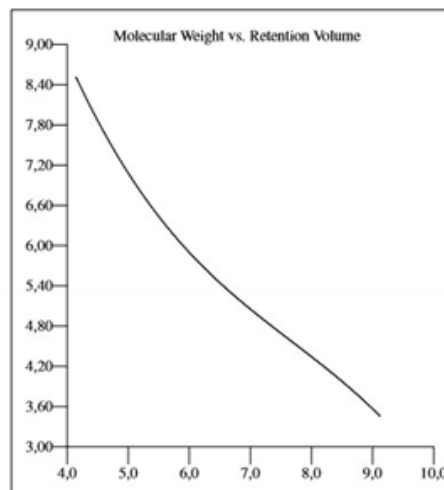
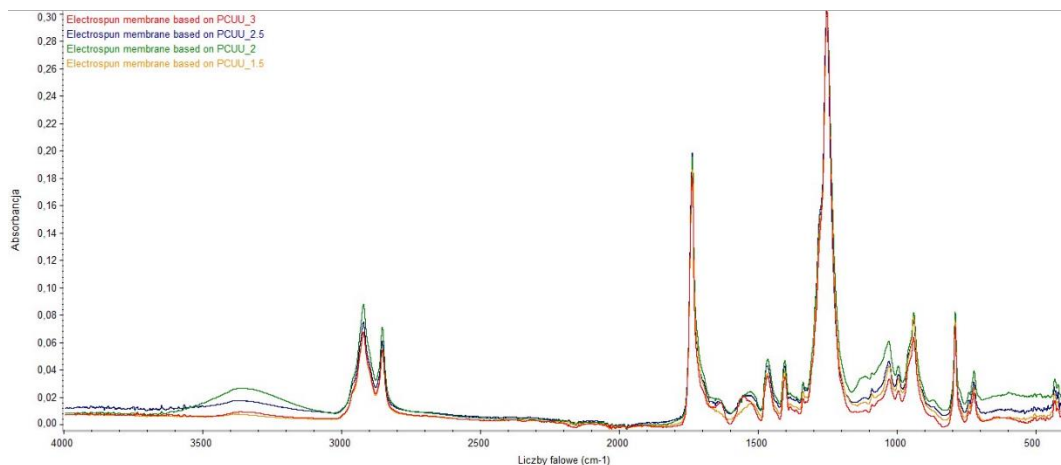
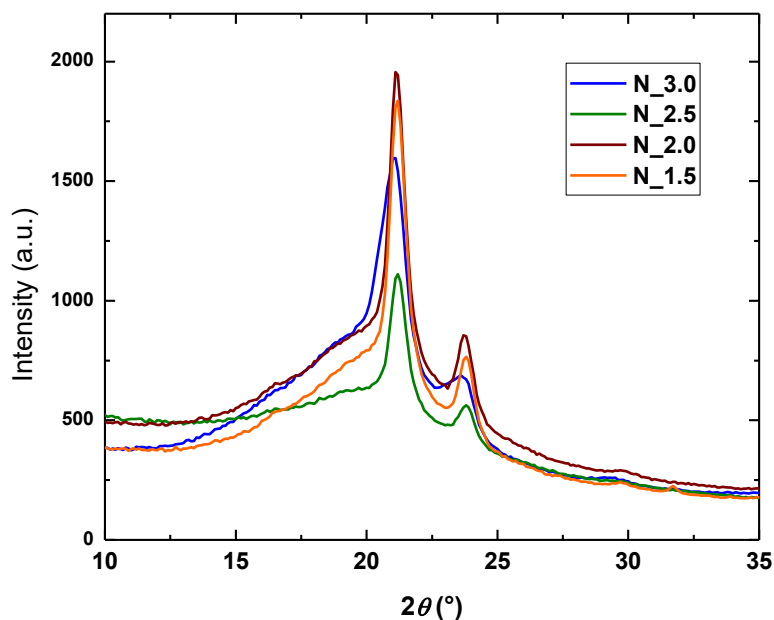


Figure S19. GPC curves of PCUU\_1.5.



**Figure S20.** ATR-FTIR spectra of spectra of N\_3 (red line), N\_2.5 (purple line), N\_2 (green line), and N\_1.5 (yellow line).



**Figure S21.** WAXS curves of scattering angle  $2\theta$  ( $^\circ$ ) for PCUU nonwovens.

**Table S3.** Average degree of crystallinity (DOC) and average crystal size ( $l_c$ ) of PCUU nonwovens determined by WAXS.

Sample	HS (wt.%)	Average DOC (%)	Average $l_c$ (nm)
N_3.0	$18 \pm 1$	$28.4 \pm 0.8$	$9.1 \pm 0.2$
N_2.5	$15 \pm 1$	$29.1 \pm 0.3$	$13.8 \pm 0.1$
N_2.0	$13 \pm 1$	$30.6 \pm 4.9$	$15.1 \pm 0.3$
N_1.5	$10 \pm 1$	$29.0 \pm 0.2$	$14.4 \pm 0.0$



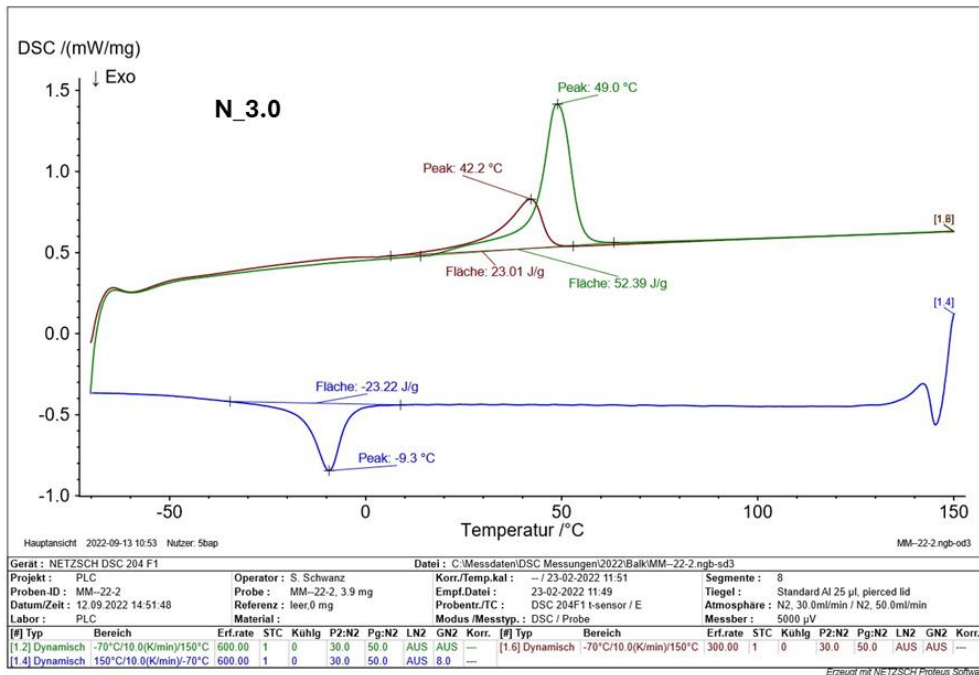


Figure S22. DSC curves of N\_3.0.

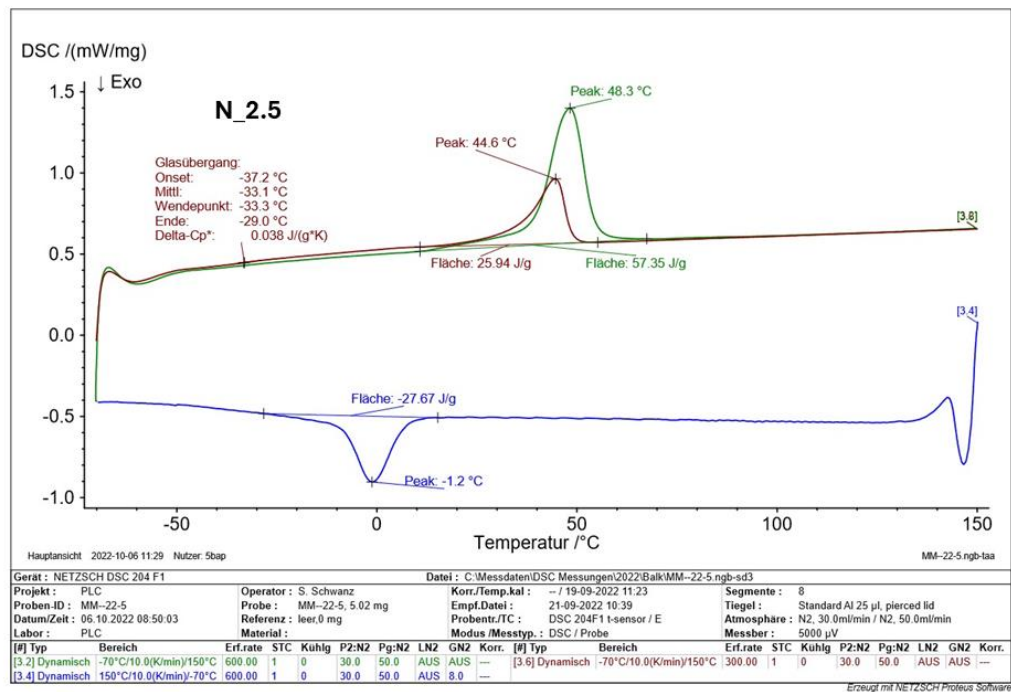


Figure S23. DSC curves of N\_2.5.

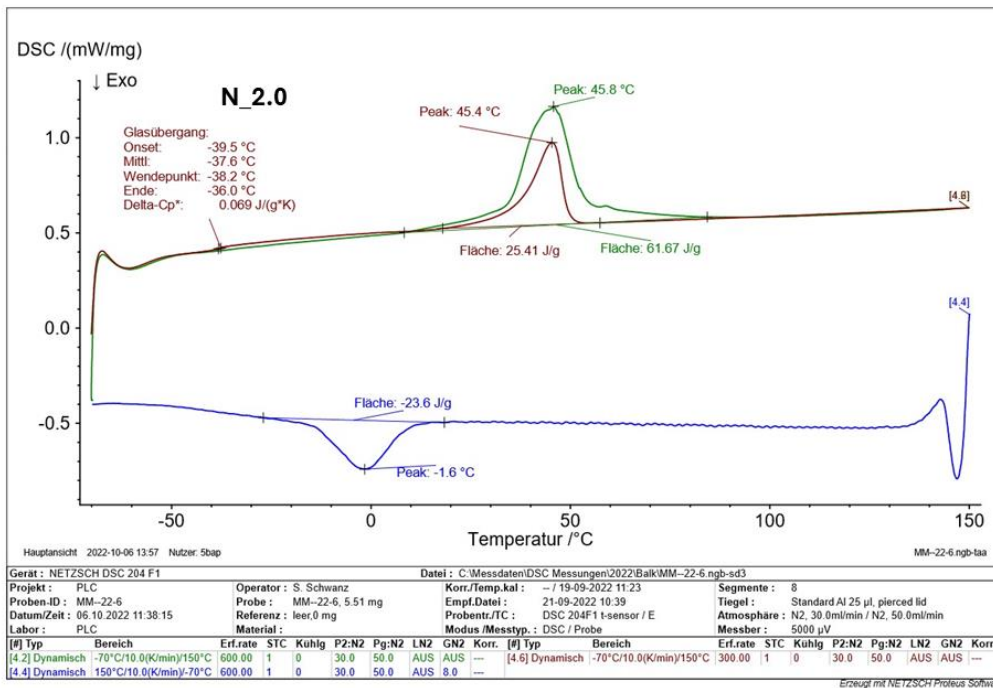


Figure S24. DSC curves of N\_2.0.

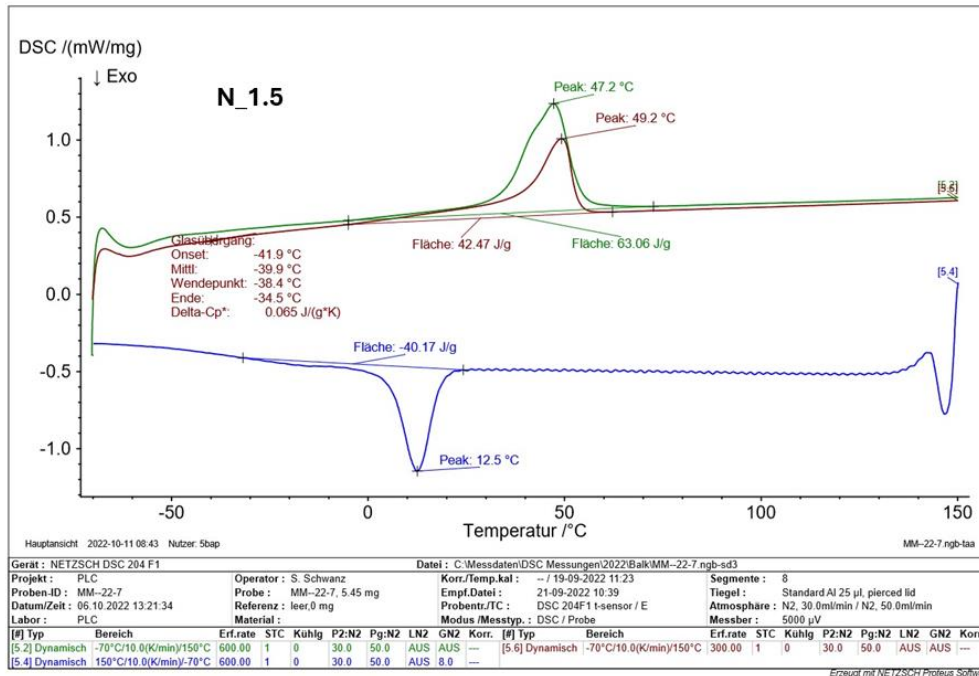


Figure S25. DSC curves of N\_1.5.

**Table S4.** Mechanical properties of PCUU nonwovens at RT and 37 °C.

<b>Temp.</b>	<b>Sample</b>	<b>HS (wt.%)</b>	<b>E (MPa)</b>	<b><math>\sigma</math> (MPa)</b>	<b><math>\epsilon</math> (%)</b>
RT	N_3.0	18 ± 1	11.83 ± 0.52	4.01 ± 0.32	288 ± 40
	N_2.5	15 ± 1	11.61 ± 2.81	3.41 ± 0.95	226 ± 39
	N_2.0	13 ± 1	2.28 ± 0.28	1.65 ± 0.12	190 ± 36
	N_1.5	10 ± 1	8.99 ± 1.31	3.35 ± 0.11	171 ± 11
37°C	N_3.0	18 ± 1	5.39 ± 1.06	2.53 ± 0.51	262 ± 75
	N_2.5	15 ± 1	3.18 ± 0.87	2.04 ± 0.32	346 ± 27
	N_2.0	13 ± 1	1.33 ± 0.14	2.40 ± 0.26	320 ± 34
	N_1.5	10 ± 1	3.30 ± 0.52	2.60 ± 0.20	264 ± 59