Electronic Supplementary Material (ESI) for RSC Applied Polymers.

Supporting Information

How introduction of hydrolyzable moieties in POx influences particle formation – A library approach based on block copolymers comprising polyesters

Natalie E. Göppert,[a,b] , Antje Vollrath,[a,b] Leanne M. Stafast, [a,b] Steffi Stumpf, [a,b] Bianca Schulze,[a,b] Stephanie Hoeppener [a,b] Christine Weber,[a,b] Ulrich S. Schubert[a,b]*

[a]Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany.

[b]Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany

EXPERIMENTAL SECTION

Synthesis of azido-terminated poly(ethylene imine-*stat*-glycine) with 15% DO, oxPEI$_{15\%}$-N$_3$

oxPEI$_{15\%}$-N$_3$ was synthesized following the general method using **PEI-N$_3$** (3.03 g, 1.68 mmol, 68.3 mmol amino units) and hydrogen peroxide solution (30% w/w, 2.31 mL, 0.33 equiv. per amino unit). **oxPEI$_{15\%}$-N$_3$** was obtained as a slightly yellow solid (3.21 g, quantitative).

$M_{n,theor.}$ = 1,900 g mol^{-1}.

^{1}H NMR (300 MHz, D_2O): δ = 8.05–7.83 (br, N*H*–CO–CH_2, glycine unit), 3.74–3.23 (br, NH–CO–C*H*$_2$, glycine unit and C*H*$_2$–C*H*$_2$, EtOx unit), 3.23–2.49 (br, NH–C*H*$_2$–C*H*$_2$, ethylene imine unit), 2.49–2.32 (br, CO–C*H*$_2$–CH_3, EtOx unit), 1.20–0.94 ppm (br, CO–CH_2–C*H*$_3$, EtOx unit); degree of oxidation (DO) = 15%.

SEC (DMAc, 0.21 wt% LiCl, RI detection, PS calibration): M_n = 2,200 g mol^{-1}; Đ = 1.75.

ART-IR: ν (N_3) = 2,099 cm^{-1}.

Synthesis of azido-terminated poly(ethylene imine-*stat*-glycine) with 32% DO, oxPEI$_{32\%}$-N$_3$

oxPEI$_{32\%}$-N$_3$ was synthesized following the general procedure using **PEI-N$_3$** (3.05 g, 1.69 mmol, 68.7 mmol amino units) and hydrogen peroxide solution (30% w/w, 3.42 mL, 0.49 equiv. per amino unit) **oxPEI$_{32\%}$-N$_3$** was obtained as a yellow solid (3.16 g, 95%).

$M_{n,theor.}$ = 2,000 g mol^{-1}.

^{1}H NMR (300 MHz, D_2O): δ = 8.06–7.81 (br, N*H*–CO–CH_2, glycine unit), 3.72–3.24 (br, NH–CO–C*H*$_2$, glycine unit and C*H*$_2$–C*H*$_2$, EtOx unit), 3.24–2.53 (br, NH–C*H*$_2$–C*H*$_2$, ethylene imine

unit), 2.53–2.23 (br, CO–CH_2–CH_3, EtOx unit), 1.19–0.94 ppm (br, CO–CH_2–CH_3, EtOx unit); DO = 32%.

SEC (DMAc, 0.21 wt% LiCl, RI detection, PS calibration): M_n = 1,500 g mol^{-1}; Đ = 1.64.

ATR-IR: ν (N_3) = 2,100 cm^{-1}.

Synthesis of azido-terminated poly(ethylene imine-*stat*-glycine) with 47% DO, oxPEI$_{47\%}$-N$_3$

oxPEI$_{47\%}$-N$_3$ was synthesized according to the general procedure using **PEI-N$_3$** (3.16 g, 1.76 mmol, 71.3 mmol amino units) and hydrogen peroxide solution (30% w/w, 5.50 mL, 0.76 equiv. per amino unit). **oxPEI$_{47\%}$-N$_3$** was obtained as a light brown solid (yield: 3.39 g, 93%).

$M_{n,theor.}$ = 2,100 g mol^{-1}.

^{1}H NMR (300 MHz, D_2O): δ = 8.08–7.84 (br, N*H*–CO–CH_2, glycine unit), 3.75–3.25 (br, NH–CO–CH_2, glycine unit and CH_2–CH_2, EtOx unit), 3.25–2.45 (br, NH–CH_2–CH_2, ethylene imine unit), 2.45–2.24 (br, CO–CH_2–CH_3, EtOx unit), 1.20–0.95 ppm (br, CO–CH_2–CH_3, EtOx unit); DO = 47%.

SEC (DMAc, 0.21 wt% LiCl, RI detection, PS calibration): M_n = 1,500 g mol^{-1}; Đ = 1.62.

ATR-IR: ν (N_3) = 2,100 cm^{-1}.

Table S1: Details on the synthesis of azido-terminated poly(2-methyl-2-oxazoline-*stat*-glycine)s and poly(2-ethyl-2-oxazoline-*stat*-glycine)s.

	m (oxPEI) [g]	n (acetyl chloride) [mmol]	V (acetyl chloride) [mL]	n (propionyl chloride) [mmol]	V (propionyl chloride) [mL]	n (NEt_3) [mmol]	V (NEt_3) [mL]	Yield [g]	Yield [%]	$M_{n,theor.}$[a] [g mol^{-1}]
dPEtOx$_{15\%}$-N$_3$	1.2	-	-	64	5.6	86	12	1.1	46	3,800
dPMeOx$_{15\%}$-N$_3$	1.2	63	4.5	-	-	86	12	1.3	63	3,300
dPEtOx$_{32\%}$-N$_3$	1.2	-	-	49	4.2	65	9	0.9	41	3,500
dMeOx$_{32\%}$-N$_3$	1.2	48	3.4	-	-	65	9	1.3	71	3,100
dPEtOx$_{47\%}$-N$_3$	1.2	-	-	36	3.1	48	6.7	1.2	66	3,200
dPMeOx$_{47\%}$-N$_3$	1.2	36	2.5	-	-	48	6.7	1.4	81	2,900

[a]Obtained by calculation using theoretical units from degree of polymerization, degree of hydrolysis and DO from ^{1}H NMR.

Table S2: Details on the synthesis of the block copolymers.

	m(dPMeOx) [mg]	n(dPMeOx) [µmol]	m(dPEtOx) [mg]	n(dPEtOx) [µmol]	m(PLA) [mg]	n(PLA) [µmol]	m(PCL) [mg]	n(PCL) [µmol]	Method *	Yield [mg]	Yield [%]	$M_{n,theor.}$[a] [kg mol^{-1}]
PEtOx-*b*-PLA	-	-	60	15	98	8.4	-	-	A	108	77	13.3
PEtOx-*b*-PCL	-	-	72	18	-	-	100	13	A	129	86	12.0
dPMeOx$_{15\%}$-*b*-PLA	55	17	-	-	109	9.3	-	-	B	115	71	12.6
dPMeOx$_{15\%}$-*b*-PCL	60	18	-	-	-	-	102	13	A	117	81	11.3
dPEtOx$_{15\%}$-*b*-PLA	-	-	60	16	103	8.8	-	-	B	53	37	13.1
dPEtOx$_{15\%}$-*b*-PCL	-	-	69	18	-	-	102	13	A	113	75	11.8
dPMeOx$_{32\%}$-*b*-PLA	50	16	-	-	106	9.0	-	-	B	116	82	12.4
dPMeOx$_{32\%}$-*b*-PCL	60	19	-	-	-	-	108	14	A	123	82	11.1
dPEtOx$_{32\%}$-*b*-PLA	-	-	100	28	185	16	-	-	A	196	77	12.8
dPEtOx$_{32\%}$-*b*-PCL	-	-	65	18	-	-	103	13	A	122	83	11.5
dPMeOx$_{47\%}$-*b*-PLA	45	16	-	-	101	8.7	-	-	A	104	78	12.2
dPMeOx$_{47\%}$-*b*-PCL	57	20	-	-	-	-	110	14	A	120	80	10.9
dPEtOx$_{47\%}$-*b*-PLA	-	-	45	14	92	7.9	-	-	B	78	64	12.5
dPEtOx$_{47\%}$-*b*-PCL	-	-	59	18	-	-	103	13	A	108	75	11.1

* Method A: Precipitation in methanol (−80 °C). Method B: Precipitation in methanol (RT). [a]Obtained by calculation using theoretical units from degree of polymerization, degree of hydrolysis and DO from ^{1}H NMR.

ADDITIONAL FIGURES DEPICTING POLYMER CHARACTERIZATION DATA

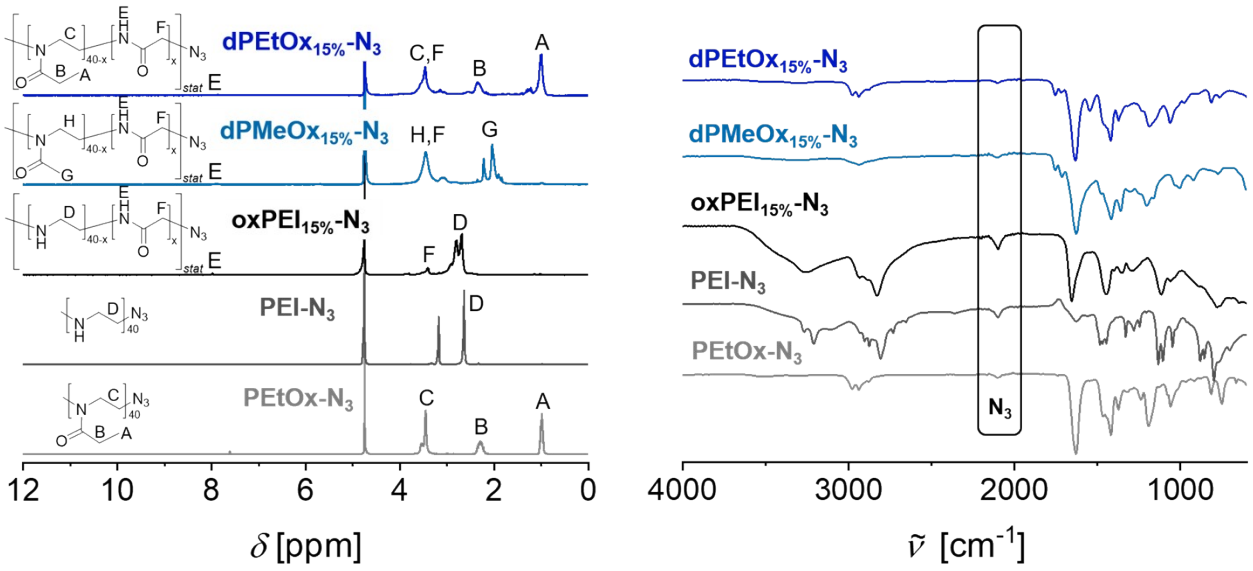

Figure SI 1: Analysis of the polymers within the synthesis sequence **PEtOx-N_3**, **PEI-N_3**, **oxPEI$_{15\%}$-N_3**, **dPMeOx$_{15\%}$-N_3** and **dPEtOx$_{15\%}$-N_3** with a DO = 15%. Left: Overlay of the ^{1}H NMR spectra (300 MHz, D_2O or MeOD) and assignment to the schematic representations of the structure of the polymer. Right: Overlay of the ATR-IR spectra (the characteristic azido vibration band is highlighted).

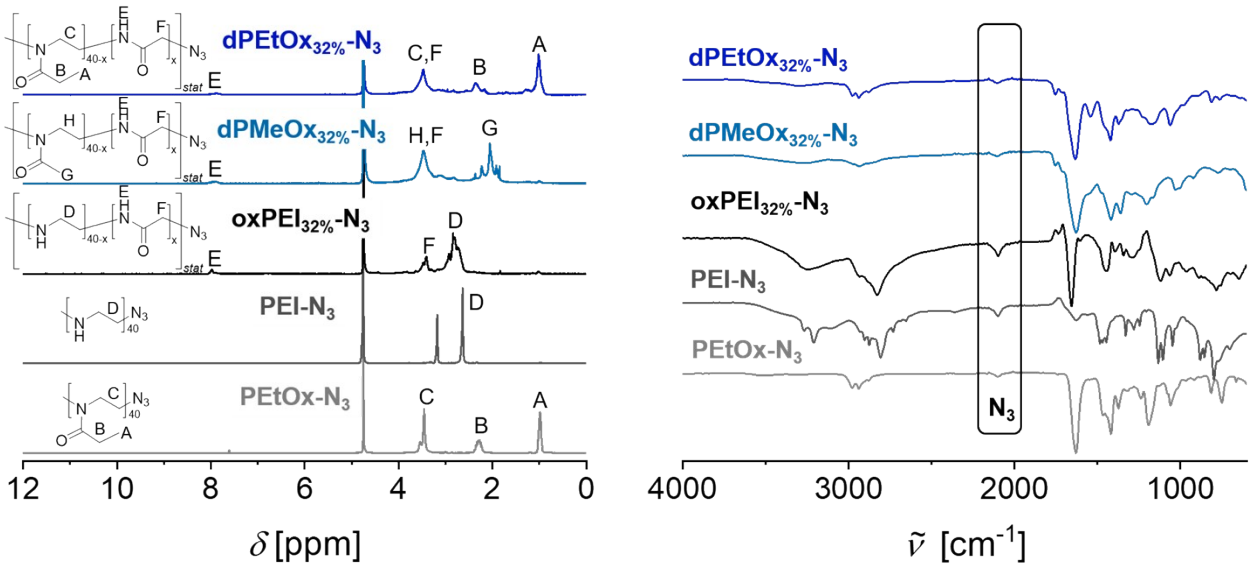

Figure SI 2: Analysis of the polymers within the synthesis sequence **PEtOx-N_3**, **PEI-N_3**, **oxPEI$_{32\%}$-N_3**, **dPMeOx$_{32\%}$-N_3** and **dPEtOx$_{32\%}$-N_3** with a DO = 32%. Left: Overlay of the ^{1}H NMR spectra (300 MHz, D_2O or MeOD) and assignment to the schematic representations of the structure of the polymer. Right: Overlay of the ATR-IR spectra (the characteristic azido vibration band is highlighted).

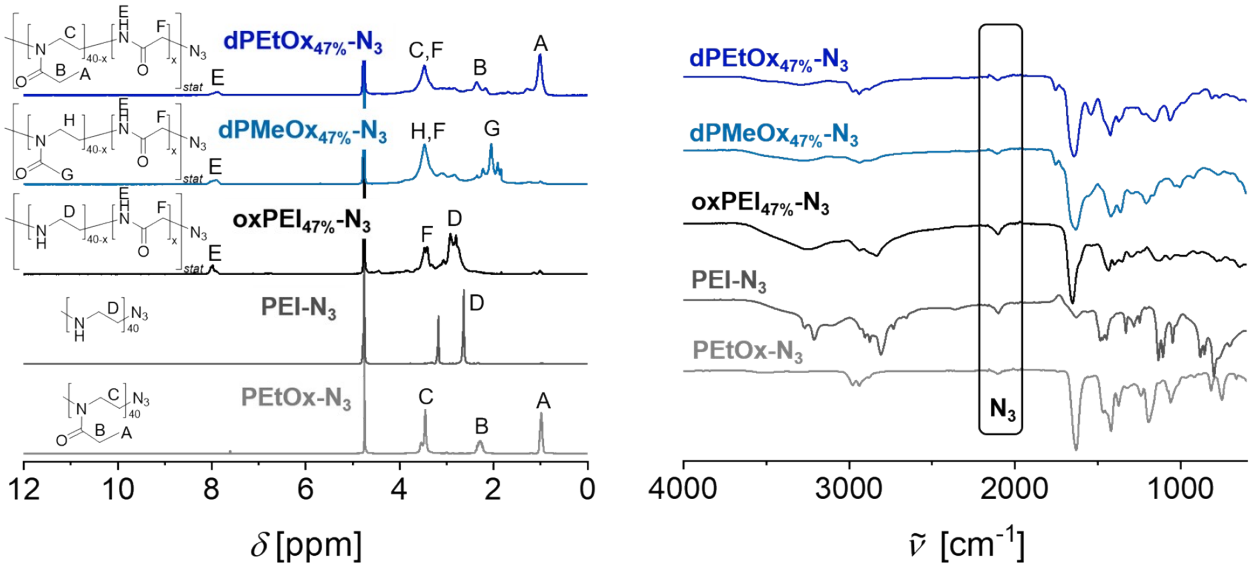

Figure SI 3: Analysis of the polymers within the synthesis sequence **PEtOx-N$_3$**, **PEI-N$_3$**, **oxPEI$_{47\%}$-N$_3$**, and **dPMeOx$_{47\%}$-N$_3$** and **dPEtOx$_{47\%}$-N$_3$** with a DO = 47%. Left: Overlay of the ^{1}H NMR spectra (300 MHz, D_2O or MeOD) and assignment to the schematic representations of the structure of the polymer. Right: Overlay of the ATR-IR spectra (the characteristic azido vibration band is highlighted).

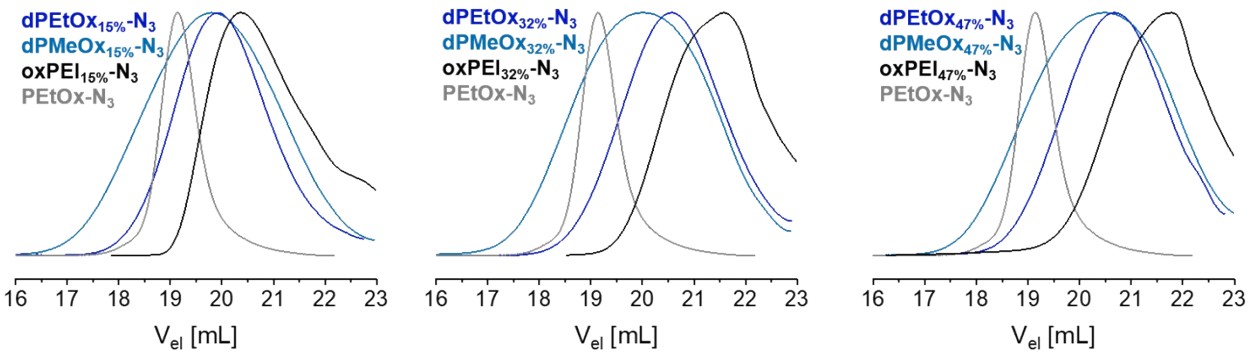

Figure SI 4: Overlay of the SEC elugrams (DMAc, RI detection) of the polymers within the synthesis sequence **PEtOx-N$_3$**, **PEI-N$_3$**, as well as the different oxPEI-N$_3$, dPMeOx-N$_3$ and dPEtOx-N$_3$ with DO = 15%, 32% and 47%, respectively.

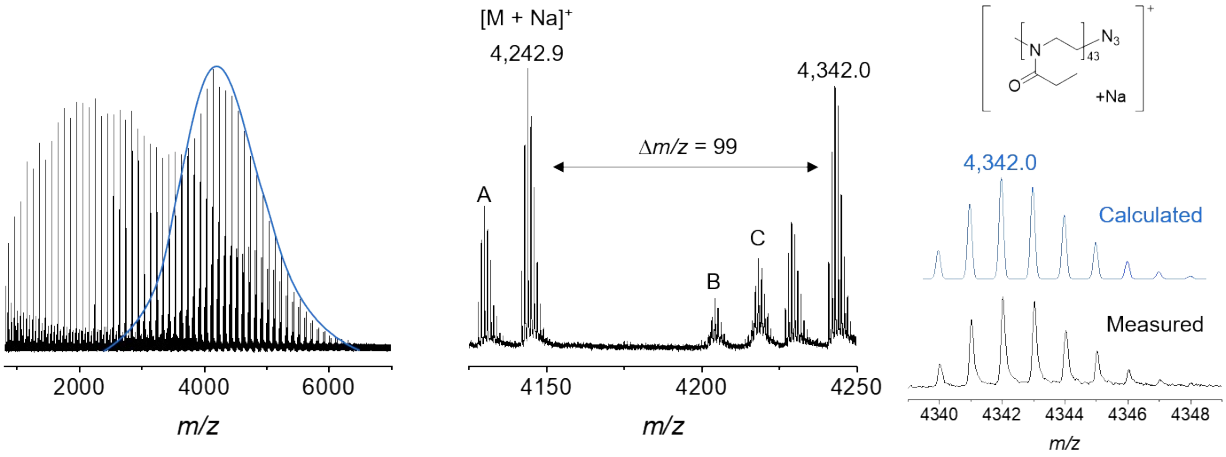

Figure SI 5: MALDI TOF MS analysis (matrix DCTB + NaTFA) of **PEtOx-N_3**. Left: Full spectrum. Middle: Zoom into the *m/z* region of one repeating unit ($\Delta m/z = 99$) with the assignment of the most abundant species (A: $[H(C_5H_9NO)_nN_3 + Na]^+$, B: $[H(C_5H_9NO)_nOH + Na]^+$ and $[H(C_5H_9NO)_nN + Na]^+$, C: $[H_3C(C_5H_9NO)_nOH + Na]^+$ and $[H_3C(C_5H_9NO)_nN + Na]^+$). Proton initiated species result from a chain transfer reaction commonly occurring in the CROP and are ionized preferably due to their lower molar mass.[1, 2] The N endgroup appeared as a result of the detachment of N_2 due to the high laser energy applied in the measurement.[3] Right: Overlay of the measured and the calculated isotopic pattern of the most prominent species ($[M + Na]^+$).

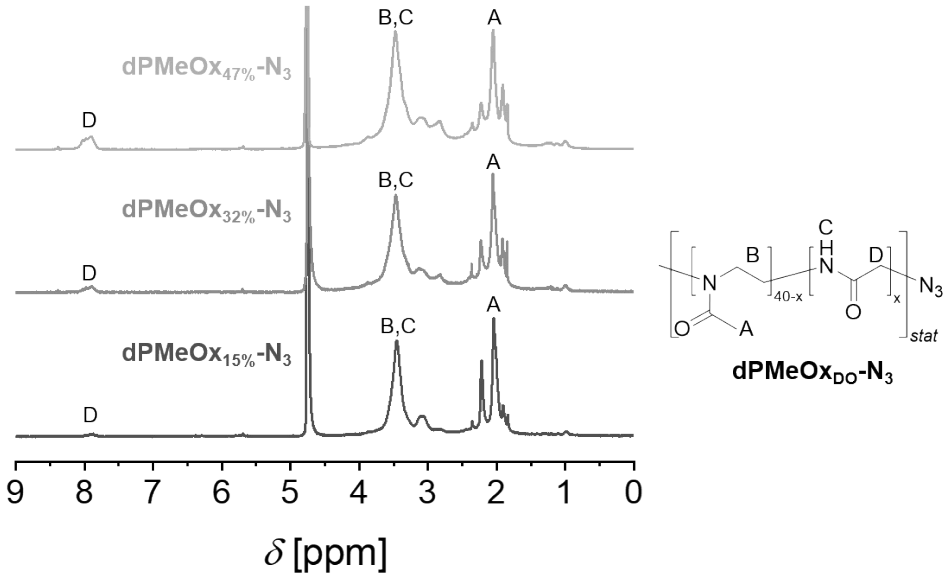

Figure SI 6: Overlay of the ^{1}H NMR spectra (300 MHz, D_2O) of the dPMeOx-N_3 with the different DO. Spectra are normalized according to the intensity of signal A.

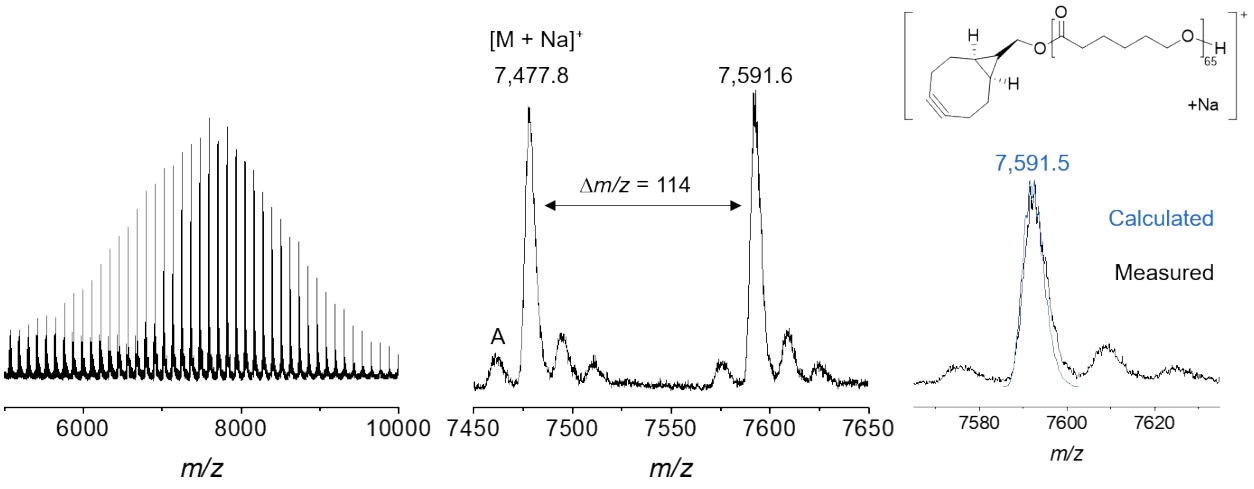

Figure SI 7: MALDI TOF MS analysis (matrix DCTB + NaI) of **BCN-PCL**. Left: Full spectrum. Middle: Zoom into the m/z region of one repeating unit ($\Delta m/z$ = 114) with the assignment of the most abundant species (A: $[HO(C_6H_{10}O_2)_nH + Na]^+$). Right: Overlay of the measured and the calculated isotopic pattern of the most prominent species ([M + Na]+).

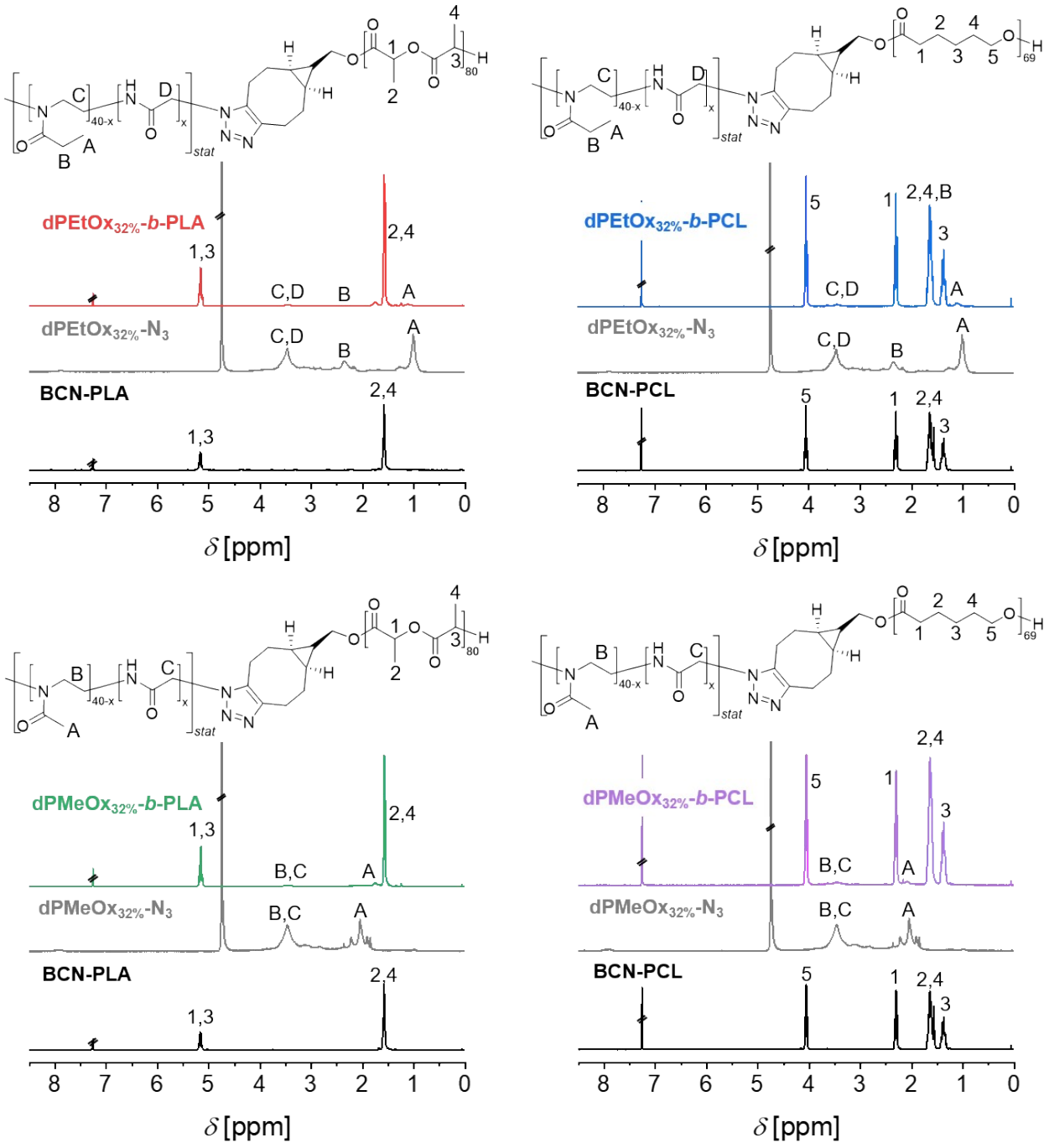

Figure SI 8: ^{1}H NMR spectra (300 MHz, D_2O or $CDCl_3$) of the block copolymers comprising dPAOx blocks with 32% DO **dPMeOx$_{32\%}$-*b*-PLA**, **dPEtOx$_{32\%}$-*b*-PLA**, **dPMeOx$_{32\%}$-*b*-PCL**, **dPEtOx$_{32\%}$-*b*-PCL** and the corresponding building blocks **dPMeOx$_{32\%}$-N$_3$**, **dPEtOx$_{32\%}$-N$_3$**, **BCN-PLA** and **BCN-PCL**, respectively, with assignment of the signals to the schematic representation of the structure.

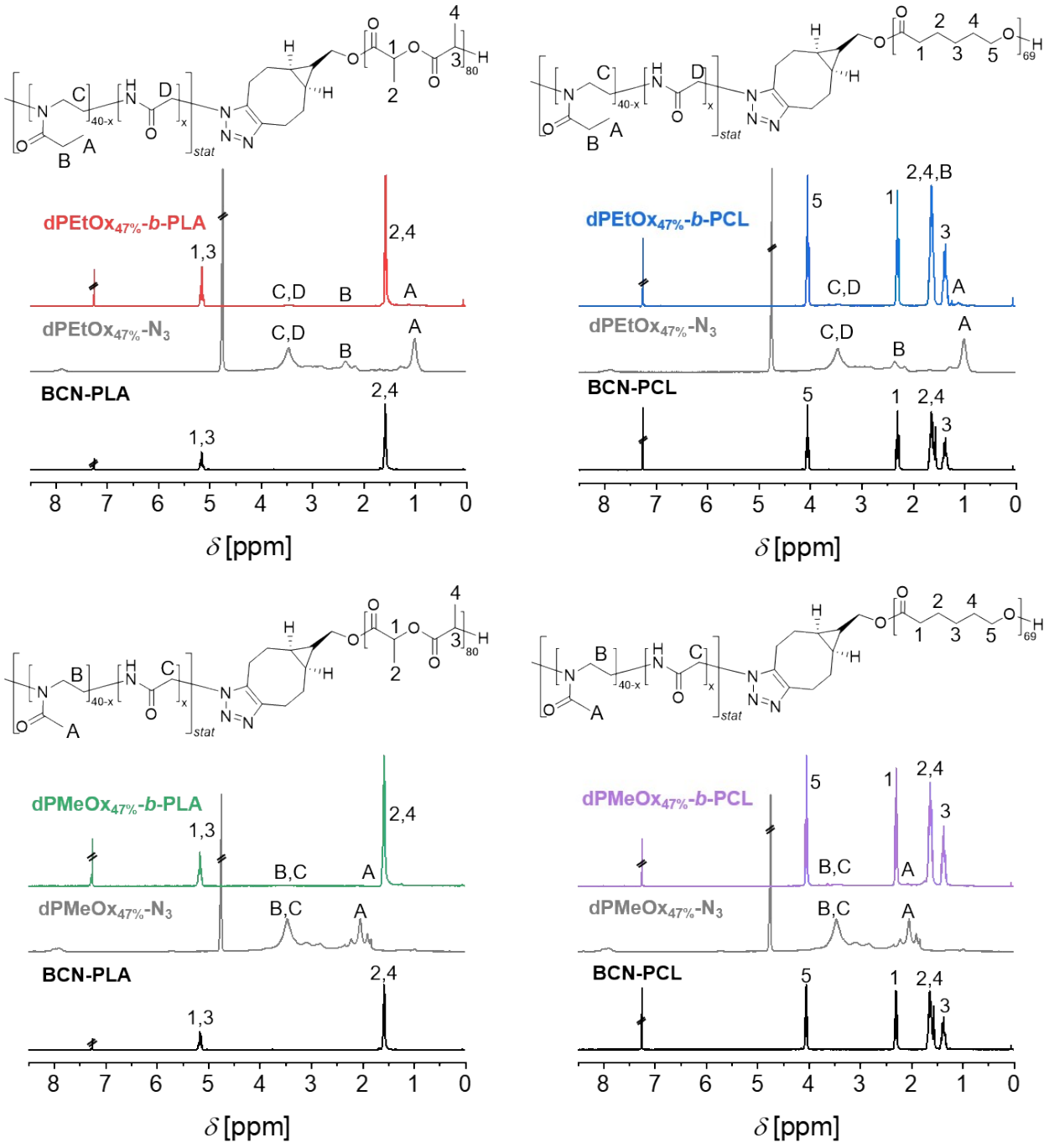

Figure SI 9: ^{1}H NMR spectra (300 MHz, D_2O or $CDCl_3$) of the block copolymers comprising dPAOx blocks with 47% DO **dPMeOx$_{47\%}$-*b*-PLA**, **dPEtOx$_{47\%}$-*b*-PLA**, **dPMeOx$_{47\%}$-*b*-PCL**, **dPEtOx$_{47\%}$-*b*-PCL** and the corresponding building blocks **dPMeOx$_{47\%}$-N$_3$**, **dPEtOx$_{47\%}$-N$_3$**, **BCN-PLA** and **BCN-PCL**, respectively, with assignment of the signals to the schematic representation of the structure.

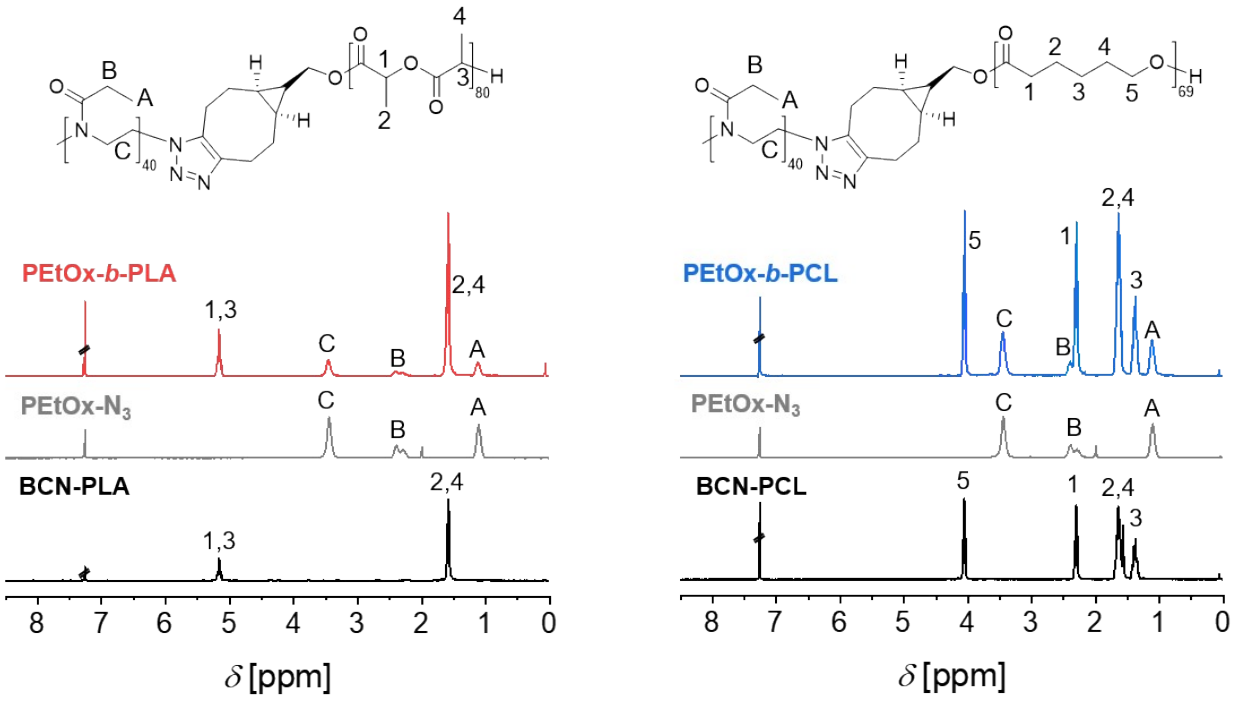

Figure SI 10: ^{1}H NMR spectra (300 MHz, $CDCl_3$) of the block copolymers **PEtOx-*b*-PLA**, **PEtOx-*b*-PCL** and the corresponding building blocks **PEtOx-N$_3$**, **BCN-PLA** and **BCN-PCL**, respectively, with assignment of the signals to the schematic representation of the structure.

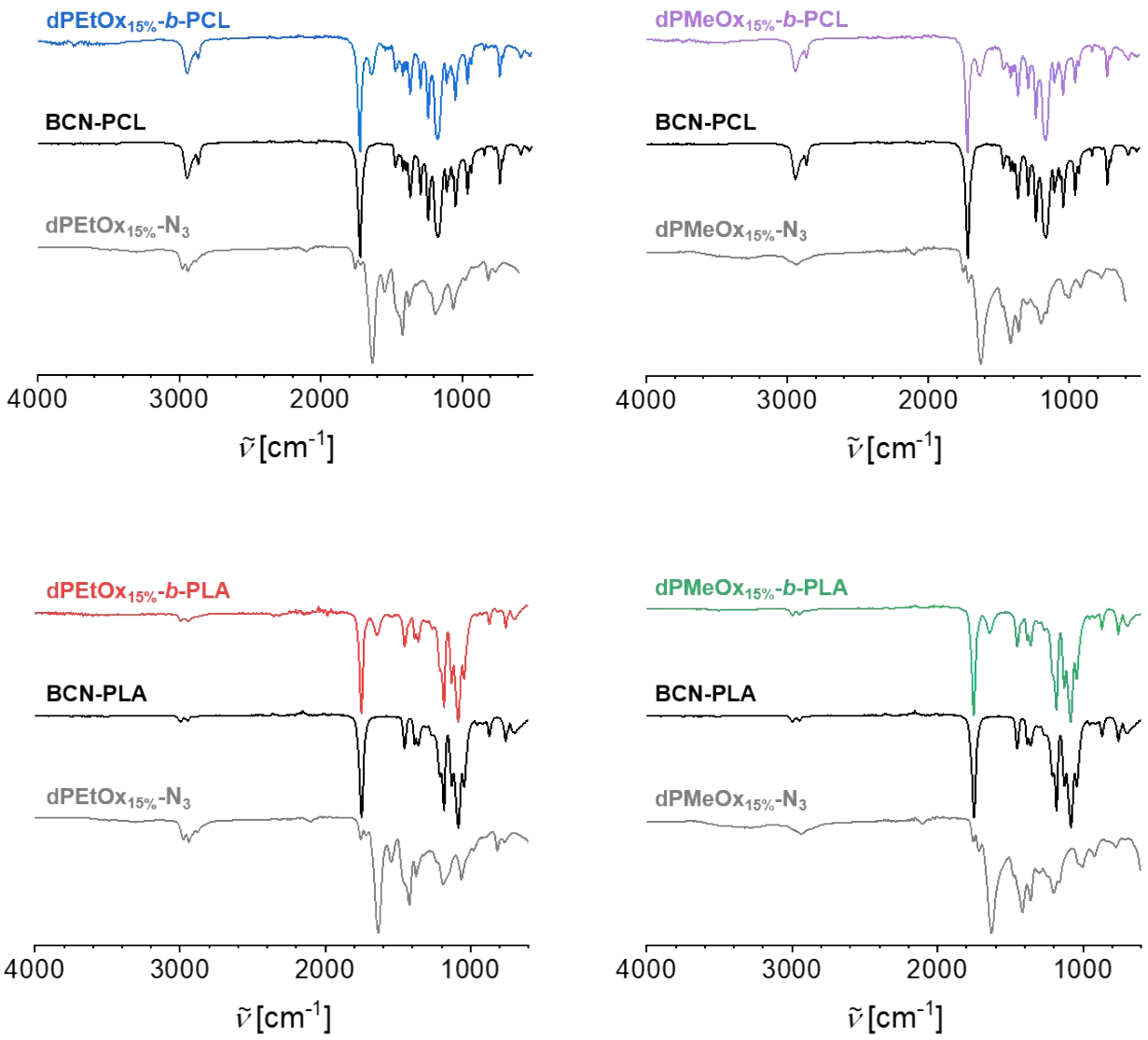

Figure SI 11: Overlay of the ATR-IR spectra of **dPMeOx$_{15\%}$-*b*-PLA**, **dPEtOx$_{15\%}$-*b*-PLA**, **dPMeOx$_{15\%}$-*b*-PCL**, **dPEtOx$_{15\%}$-*b*-PCL** and the corresponding building blocks **dPMeOx$_{15\%}$-N$_3$**, **dPEtOx$_{15\%}$-N$_3$**, **BCN-PLA** and **BCN-PCL**, respectively.

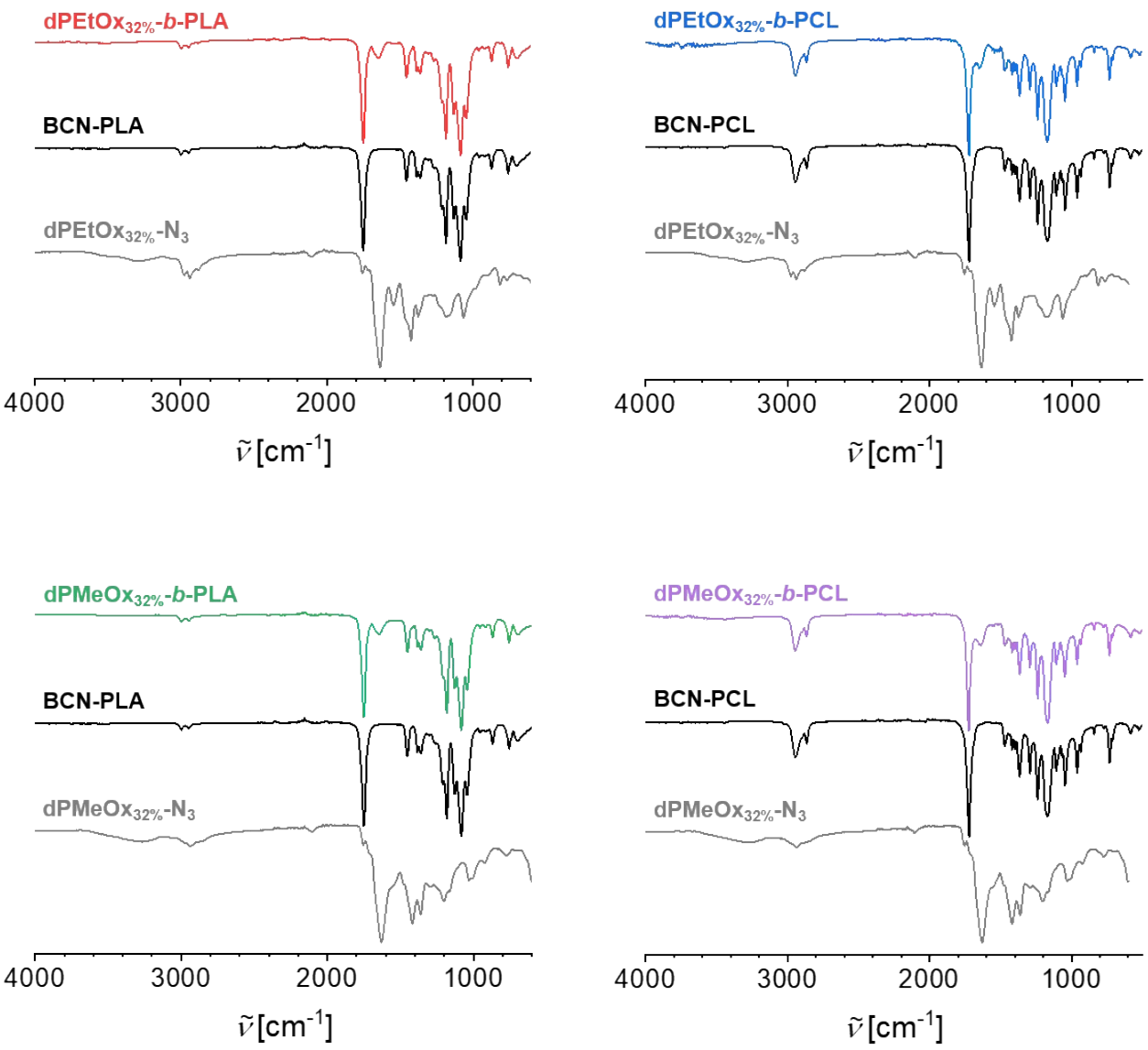

Figure SI 12: Overlay of the ATR-IR spectra of **dPMeOx$_{32\%}$-*b*-PLA**, **dPEtOx$_{32\%}$-*b*-PLA**, **dPMeOx$_{32\%}$-*b*-PCL**, **dPEtOx$_{32\%}$-*b*-PCL** and the corresponding building blocks **dPMeOx$_{32\%}$-N$_3$**, **dPEtOx$_{32\%}$-N$_3$**, **BCN-PLA** and **BCN-PCL**, respectively.

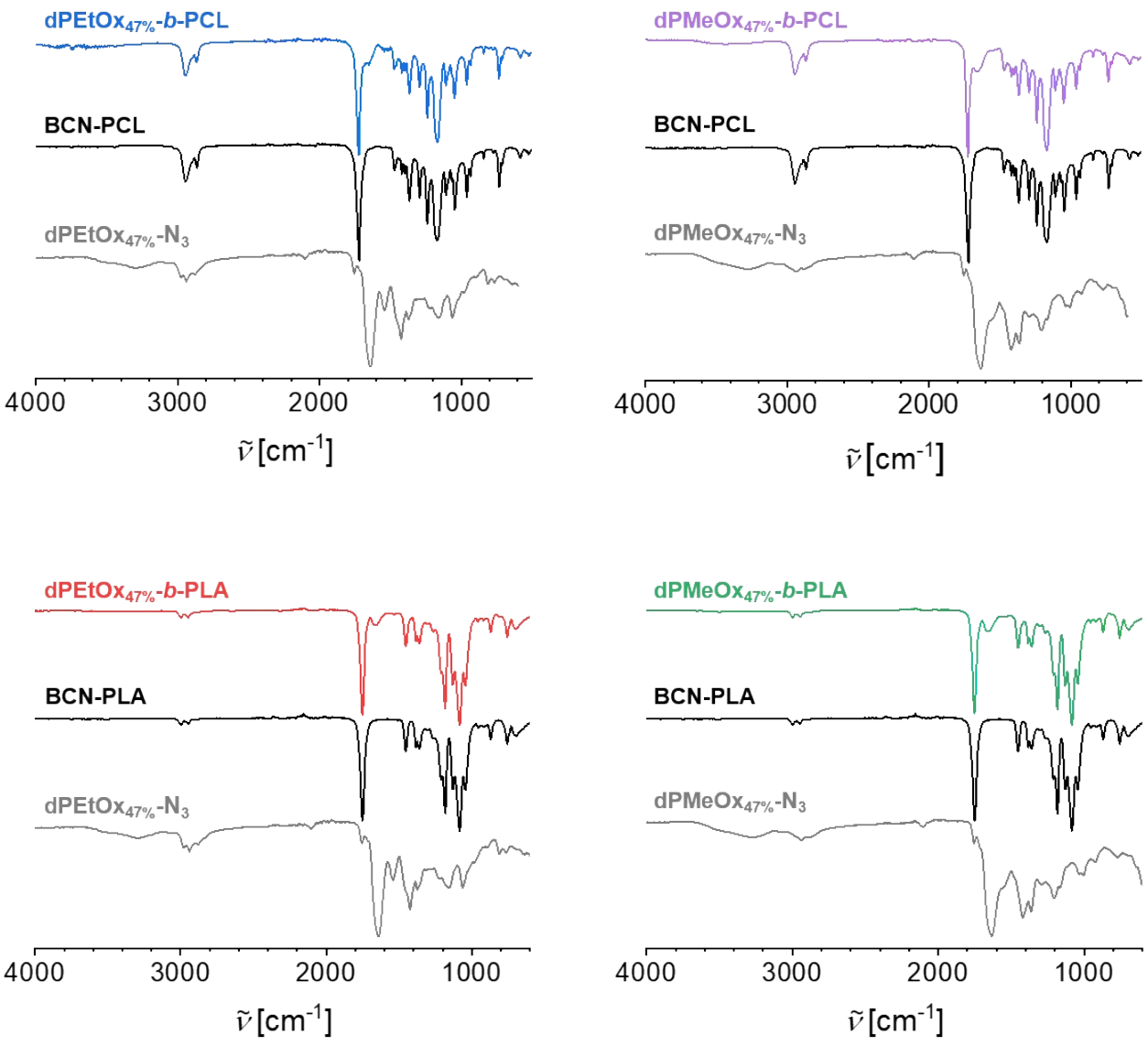

Figure SI 13: Overlay of the ATR-IR spectra of **dPMeOx$_{47\%}$-*b*-PLA**, **dPEtOx$_{47\%}$-*b*-PLA**, **dPMeOx$_{47\%}$-*b*-PCL**, **dPEtOx$_{47\%}$-*b*-PCL** and the corresponding building blocks **dPMeOx$_{47\%}$-N$_3$**, **dPEtOx$_{47\%}$-N$_3$**, **BCN-PLA** and **BCN-PCL**, respectively.

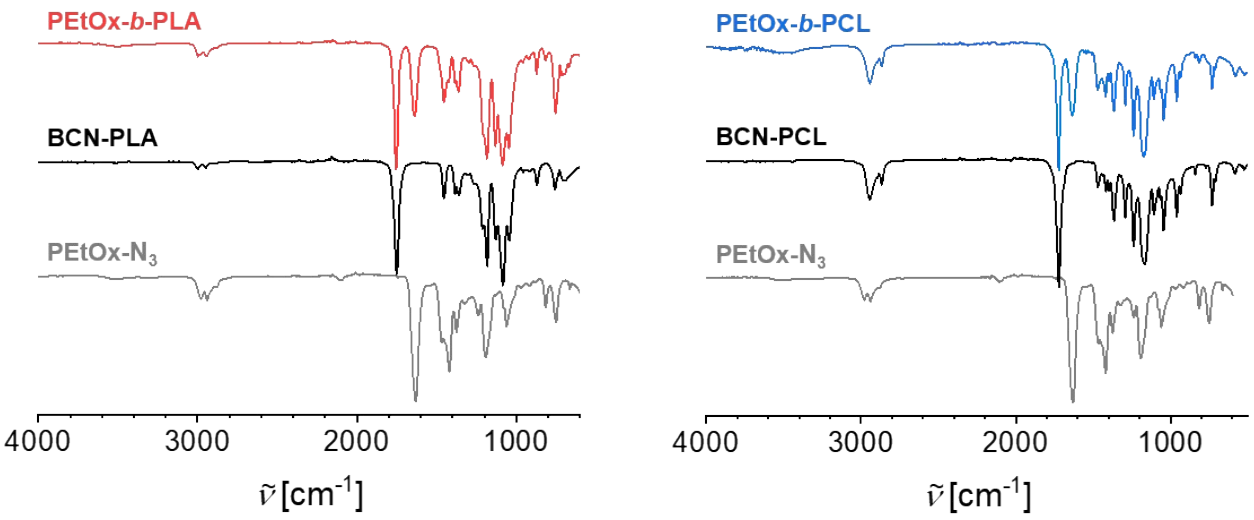

Figure SI 14: Overlay of the ATR-IR spectra of **PEtOx-*b*-PLA**, **PEtOx-*b*-PCL** and their building blocks **PEtOx-N_3**, **BCN-PLA** and **BCN-PCL**, respectively.

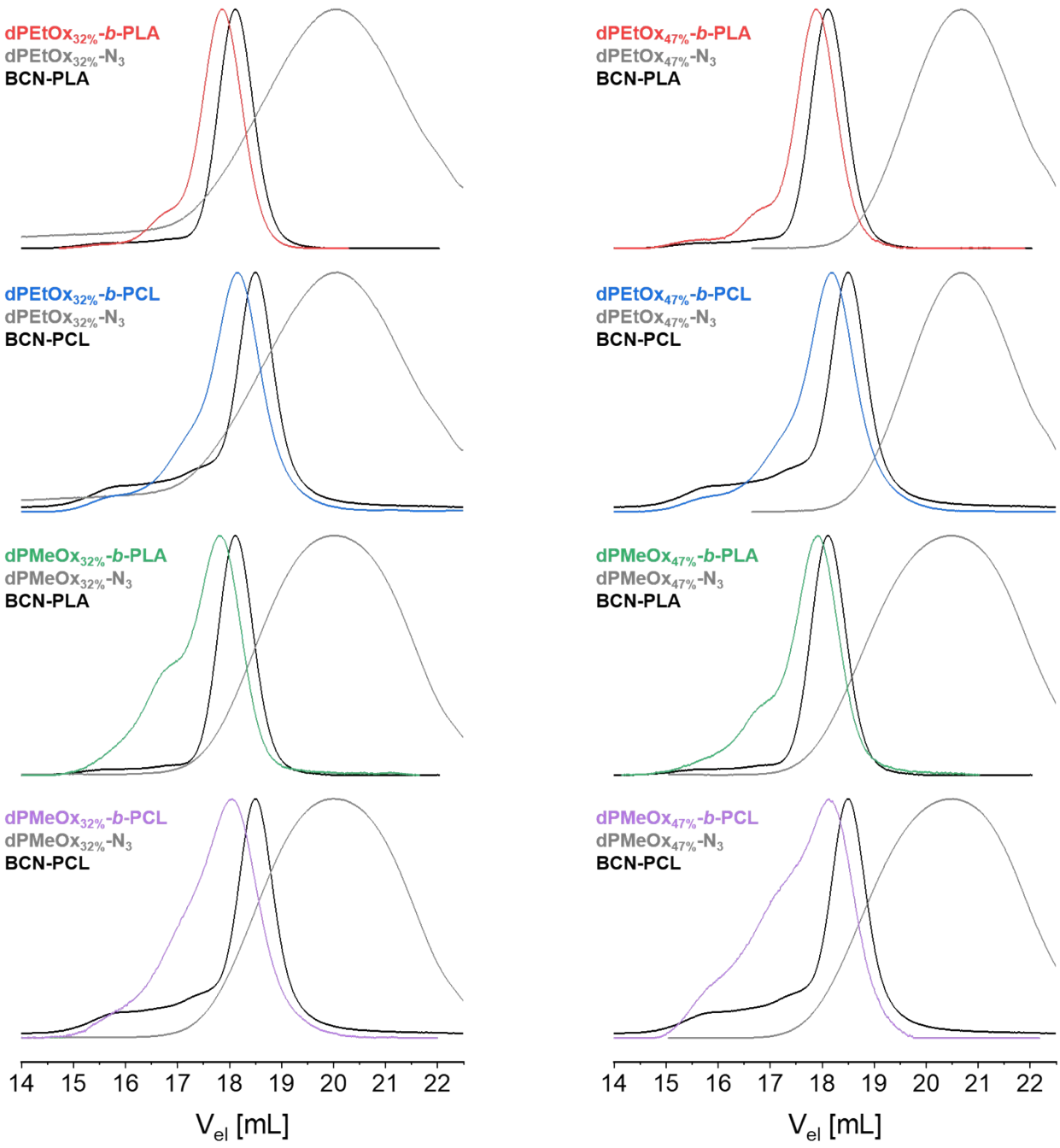

Figure SI 15: Overlay of the SEC elugrams (DMAc, RI detection) of the dPAOx-*b*-polyester block copolymers comprising dPAOx with 32% (left) and 47% (right) DO and the corresponding building blocks **dPMeOx-N$_3$**, **dPEtOx-N$_3$**, **BCN-PLA** and **BCN-PCL**.

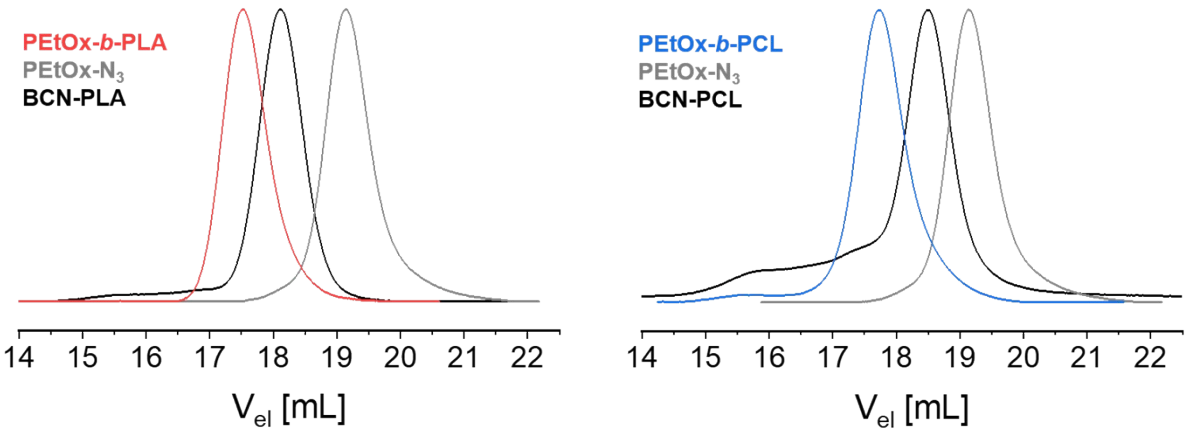

Figure SI 16: Overlay of the SEC elugrams (DMAc, RI detection) of the PEtOx-*b*-polyester block copolymers and the corresponding building blocks **PEtOx-N$_3$**, **BCN-PLA** and **BCN-PCL**.

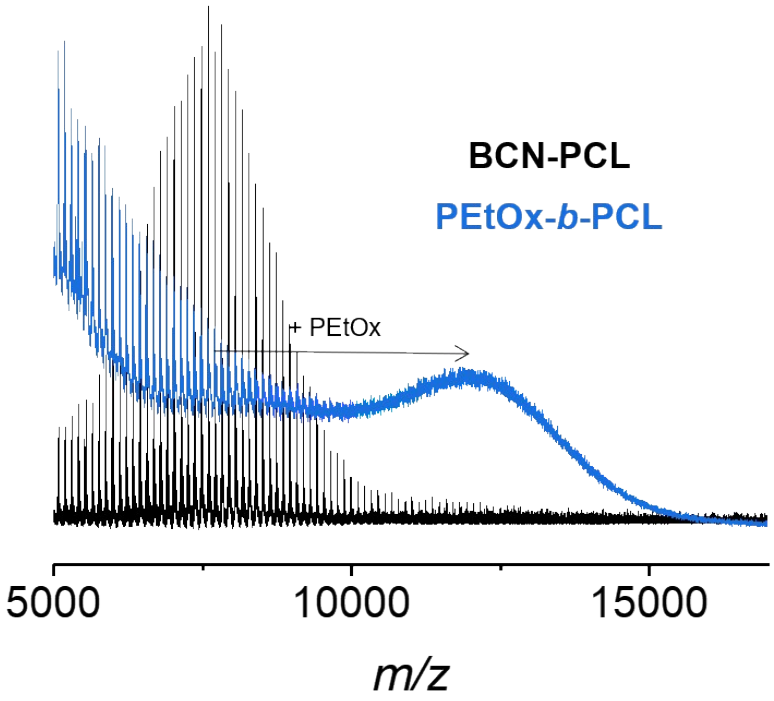

Figure SI 17: Overlay of the MALDI TOF mass spectra (matrix: **PEtOx-*b*-PCL**: DHB, **BCN-PCL**: DCTB + NaI)) of **PEtOx-*b*-PCL** and **BCN-PCL** clearly displaying a shift towards higher *m/z* values, which correlates with the molar mass of **PEtOx-N$_3$**.

Nanoparticle data

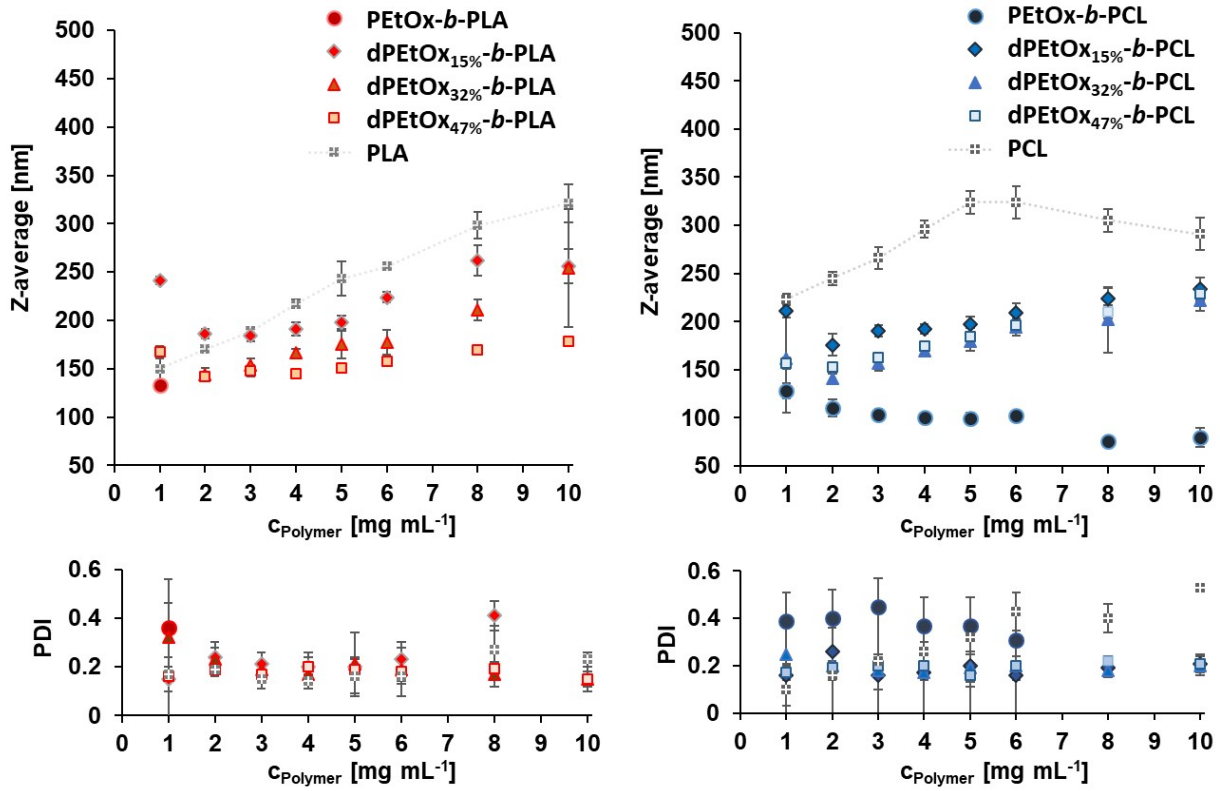

Figure SI 18: Mean particle sizes (z-average values) of the dPEtOx-*b*-polyesters, PEtOx-*b*-polyesters as well as PLA and PCL homopolymers (highlighted *via* dotted line) for n = 6 individual formulations. The z-average values are plotted in dependency of the initial polymer concentration used for the HT-formulation. No SD bars are shown if they fall into the symbol.

Table SI 1: Results of the size measurements including z-average values (d in nm, upper table) and the corresponding polydispersity index (PDI, lower table) of dPEtOx-*b*-PLA particle formulations (n = 6 individual formulations, standard deviation (SD) values represent variation between these 6 independent formulations).

Polymer	**PEtOx-*b*-PLA**			**dPEtOx$_{15\%}$-*b*-PLA**			**dPEtOx$_{32\%}$-*b*-PLA**			**dPEtOx$_{47\%}$-*b*-PLA**			**PLA**		
c (mg mL^{-1})	d (nm)		SD	d (nm)		SD	d (nm)		SD	d (nm)		SD	d (nm)		SD
1.00	**133**	±	16	**241**	±	4	**470**	±	351	**167**	±	6	**150**	±	12
2.00	#			**186**	±	5	**144**	±	7	**142**	±	4	**170**	±	3
3.00	#			**184**	±	6	**154**	±	7	**148**	±	6	**189**	±	5
4.00	#			**191**	±	7	**166**	±	4	**145**	±	3	**217**	±	3
5.00	#			**198**	±	7	**175**	±	14	**151**	±	3	**243**	±	18
6.00	#			**224**	±	5	**177**	±	13	**158**	±	4	**256**	±	4
8.00	#			**262**	±	16	**211**	±	11	**169**	±	5	**298**	±	14
10.00	#			**256**	±	18	**254**	±	61	**178**	±	4	**321**	±	20
c (mg mL^{-1})	PDI		SD	PDI		SD	PDI		SD	PDI		SD	PDI		SD
1.00	**0.36**	±	0.20	**0.15**	±	0.05	**0.32**	±	0.14	**0.16**	±	0.02	**0.17**	±	0.07
2.00	#			**0.24**	±	0.04	**0.23**	±	0.07	**0.19**	±	0.03	**0.19**	±	0.03
3.00	#			**0.21**	±	0.05	**0.19**	±	0.03	**0.17**	±	0.02	**0.15**	±	0.04
4.00	#			**0.20**	±	0.04	**0.17**	±	0.04	**0.20**	±	0.06	**0.14**	±	0.03
5.00	#			**0.20**	±	0.04	**0.21**	±	0.13	**0.19**	±	0.04	**0.16**	±	0.07
6.00	#			**0.23**	±	0.05	**0.19**	±	0.11	**0.18**	±	0.04	**0.16**	±	0.03
8.00	#			**0.41**	±	0.06	**0.17**	±	0.05	**0.19**	±	0.02	**0.27**	±	0.10
10.00	#			#			**0.15**	±	0.05	**0.15**	±	0.03	**0.23**	±	0.03

Data not available due to aggregation, no reliable particle formulation or sufficient particle concentration.

Table SI 2: Results of the size measurements including z-average values (d in nm, upper table) and the corresponding polydispersity index (PDI, lower table) of dPEtOx-*b*-PLA particle formulations (n = 6 individual formulations, SD values represent variation between these 6 independent formulations).

Polymer	**PEtOx-*b*-PCL**			**dPEtOx$_{15\%}$-*b*-PCL**			**dPEtOx$_{32\%}$-*b*-PCL**			**dPEtOx$_{47\%}$-*b*-PCL**			**PCL**		
c (mg mL^{-1})	d (nm)		SD	d (nm)		SD	d (nm)		SD	d (nm)		SD	d (nm)		SD
1.00	**128**	±	8	**211**	±	7	**162**	±	57	**157**	±	6	**223**	±	6
2.00	**110**	±	9	**176**	±	11	**141**	±	5	**153**	±	3	**245**	±	7
3.00	**103**	±	6	**190**	±	6	**157**	±	8	**163**	±	4	**266**	±	11
4.00	**100**	±	3	**192**	±	5	**170**	±	5	**175**	±	3	**296**	±	9
5.00	**99**	±	6	**197**	±	8	**179**	±	9	**184**	±	9	**324**	±	12
6.00	**102**	±	3	**209**	±	10	**194**	±	9	**196**	±	6	**324**	±	17
8.00	#			**224**	±	11	**202**	±	34	**210**	±	7	**305**	±	12
10.00	#			**234**	±	12	**222**	±	11	**229**	±	8	**291**	±	17
c (mg mL^{-1})	PDI		SD	PDI		SD	PDI		SD	PDI		SD	PDI		SD
1.00	**0.39**	±	0.12	**0.16**	±	0.05	**0.25**	±	0.11	**0.17**	±	0.03	**0.10**	±	0.07
2.00	**0.40**	±	0.10	**0.26**	±	0.10	**0.20**	±	0.05	**0.19**	±	0.03	**0.16**	±	0.02
3.00	**0.45**	±	0.06	**0.16**	±	0.06	**0.18**	±	0.03	**0.20**	±	0.02	**0.22**	±	0.03
4.00	**0.37**	±	0.09	**0.17**	±	0.03	**0.17**	±	0.03	**0.20**	±	0.06	**0.26**	±	0.04
5.00	**0.37**	±	0.06	**0.20**	±	0.06	**0.19**	±	0.06	**0.16**	±	0.05	**0.32**	±	0.07
6.00	**0.31**	±	0.05	**0.16**	±	0.02	**0.20**	±	0.04	**0.20**	±	0.04	**0.43**	±	0.08
8.00	#			**0.19**	±	0.03	**0.18**	±	0.03	**0.22**	±	0.02	**0.40**	±	0.06
10.00	#			**0.21**	±	0.04	**0.20**	±	0.04	**0.21**	±	0.03	**0.53**	±	0.01

Data not available due to aggregation, no reliable particle formulation or sufficient particle concentration.

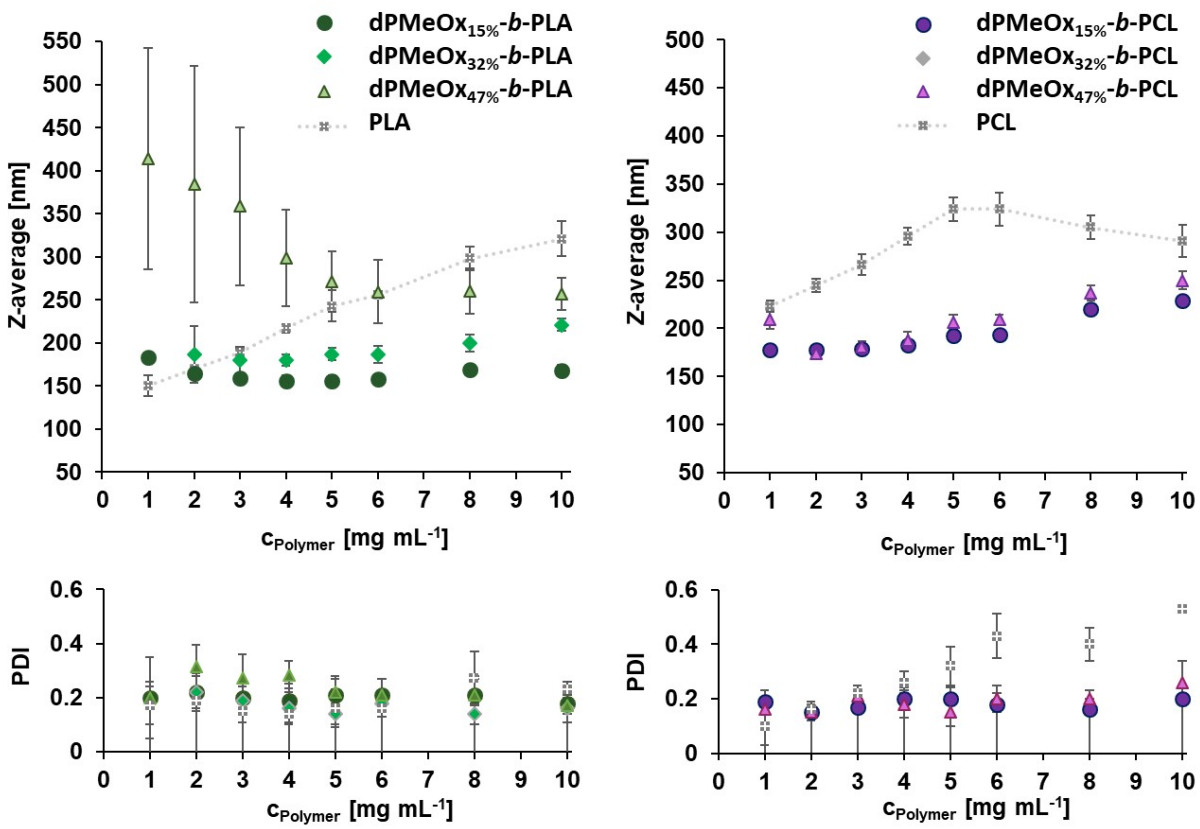

Figure SI 19: Mean particle sizes (z-average value) of the dPMeOx-*b*-polyesters as well as PLA and PCL homopolymers (highlighted *via* dotted line) for n = 6 individual formulations. The z-average values are plotted in dependency of the initial polymer concentration used for the HT-formulation. No SD bars are shown if they fall into the symbol.

Table SI 3: Results of the size measurements including z-average values (d in nm, upper table) and the corresponding polydispersity index (PDI, lower table) of dPMeOx-*b*-PLA particle formulations (n = 6 individual formulations, SD values represent variation between these 6 independent formulations).

Polymer	**dPMeOx$_{15\%}$-*b*-PLA**			**dPMeOx$_{32\%}$-*b*-PLA**			**dPMeOx$_{47\%}$-*b*-PLA**			**PLA**		
c (mg mL^{-1})	d (nm)		SD	d (nm)		SD	d (nm)		SD	d (nm)		SD
1.00	**183**	±	6	**502**	±	427	**414**	±	129	**150**	±	12
2.00	**165**	±	5	**187**	±	33	**384**	±	137	**170**	±	2
3.00	**159**	±	4	**180**	±	15	**359**	±	92	**189**	±	4
4.00	**156**	±	4	**180**	±	7	**298**	±	56	**217**	±	5
5.00	**156**	±	4	**187**	±	7	**271**	±	35	**243**	±	18
6.00	**158**	±	6	**187**	±	10	**259**	±	37	**256**	±	4
8.00	**169**	±	6	**200**	±	10	**260**	±	26	**298**	±	14
10.00	**168**	±	4	**221**	±	7	**257**	±	19	**321**	±	20

c (mg mL^{-1})	PDI		SD	PDI		SD	PDI		SD	PDI		SD
1.00	**0.20**	±	0.06	**0.21**	±	0.07	**0.20**	±	0.15	**0.17**	±	0.07
2.00	**0.22**	±	0.05	**0.22**	±	0.07	**0.32**	±	0.08	**0.19**	±	0.03
3.00	**0.20**	±	0.04	**0.19**	±	0.05	**0.27**	±	0.09	**0.15**	±	0.04
4.00	**0.19**	±	0.02	**0.16**	±	0.06	**0.28**	±	0.05	**0.14**	±	0.03
5.00	**0.21**	±	0.06	**0.14**	±	0.04	**0.22**	±	0.06	**0.16**	±	0.07
6.00	**0.21**	±	0.04	**0.18**	±	0.03	**0.21**	±	0.06	**0.16**	±	0.03
8.00	**0.21**	±	0.03	**0.14**	±	0.04	**0.21**	±	0.07	**0.27**	±	0.10
10.00	**0.18**	±	0.04	**0.16**	±	0.05	**0.17**	±	0.03	**0.23**	±	0.03

Table SI 4: Results of the size measurements including z-average values (d in nm, upper table) and the corresponding polydispersity index (PDI, lower table) of dPMeOx-*b*-PCL particle formulations (n = 6 individual formulations, SD values represent variation between these 6 independent formulations).

Polymer	**dPMeOx$_{15\%}$-*b*-PCL**			**dPMeOx$_{32\%}$-*b*-PCL**			**dPMeOx$_{47\%}$-*b*-PCL**			**PCL**		
c (mg mL^{-1})	d (nm)		SD	d (nm)		SD	d (nm)		SD	d (nm)		SD
1.00	**178**	±	3	667	±	90	**209**	±	10	**223**	±	6
2.00	**178**	±	1	809	±	51	**174**	±	4	**245**	±	7
3.00	**179**	±	3	#			**181**	±	6	**266**	±	11
4.00	**183**	±	7	773	±	270	**188**	±	8	**296**	±	9
5.00	**193**	±	7	509	±	117	**206**	±	8	**324**	±	12
6.00	**194**	±	9	759	±	334	**209**	±	5	**324**	±	17
8.00	**220**	±	9	968	±	240	**237**	±	8	**305**	±	12
10.00	**229**	±	7	#			**250**	±	9	**291**	±	17

c (mg mL^{-1})	PDI		SD	PDI			PDI		SD	PDI		SD
1.00	**0.19**	±	0.04	0.35	±	0.00	**0.16**	±	0.02	**0.10**	±	0.07
2.00	**0.15**	±	0.02	0.38	±	0.00	**0.15**	±	0.03	**0.16**	±	0.02
3.00	**0.17**	±	0.03	0.53	±	0.02	**0.21**	±	0.02	**0.22**	±	0.03
4.00	**0.20**	±	0.04	0.47	±	0.02	**0.18**	±	0.05	**0.26**	±	0.04
5.00	**0.20**	±	0.02	#			**0.15**	±	0.05	**0.32**	±	0.07
6.00	**0.18**	±	0.04	0.47	±	0.00	**0.20**	±	0.05	**0.43**	±	0.08
8.00	**0.16**	±	0.06	#			**0.20**	±	0.03	**0.40**	±	0.06
10.00	**0.20**	±	0.02	#			**0.26**	±	0.08	**0.53**	±	0.01

Data not available due to aggregation or no reliable particle formulation.

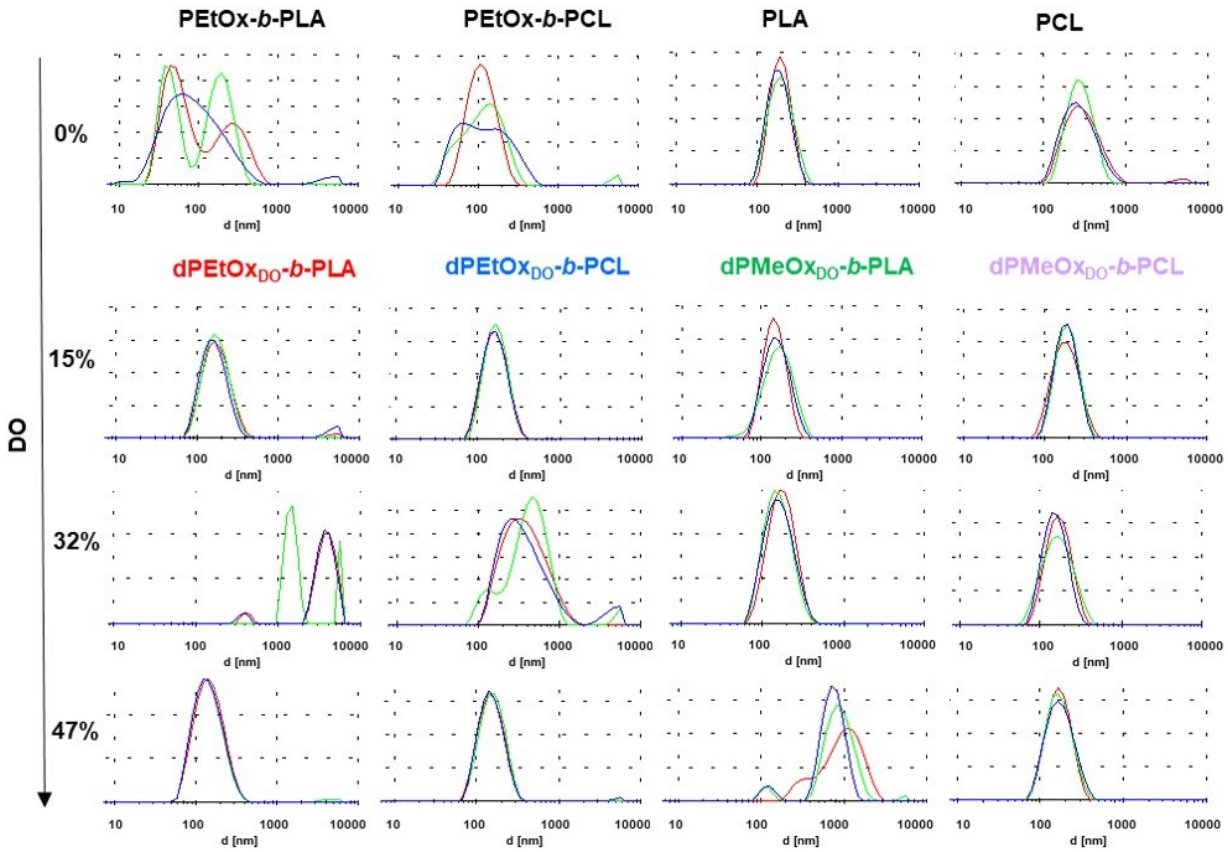

Figure SI 20: Intensity based size distributions of particles suspensions prepared with 3 mg mL^{-1} concentration in dependency of the degree of oxidation.

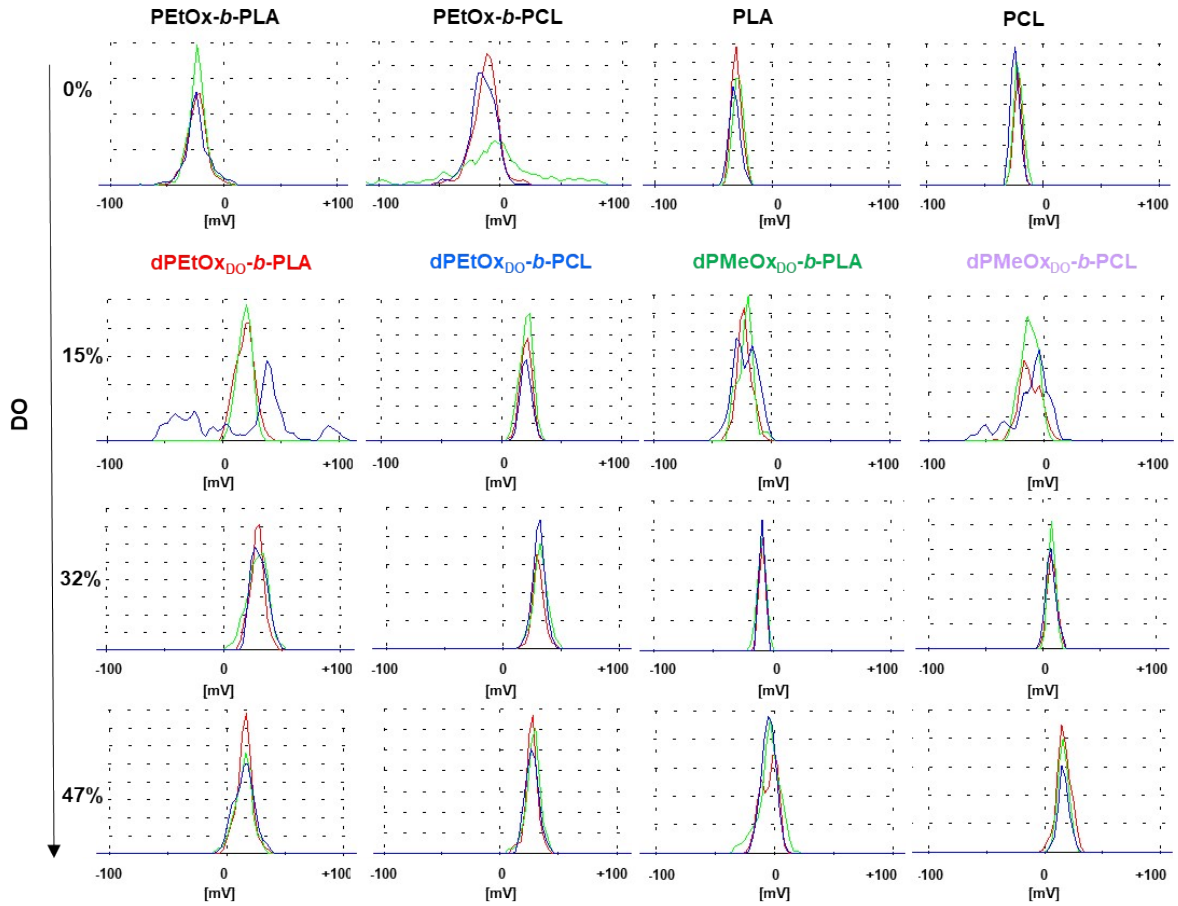

Figure SI 21: Zeta potential graphs of particles suspensions prepare with 3 mg mL^{-1} concentration in dependency of the degree of oxidation.

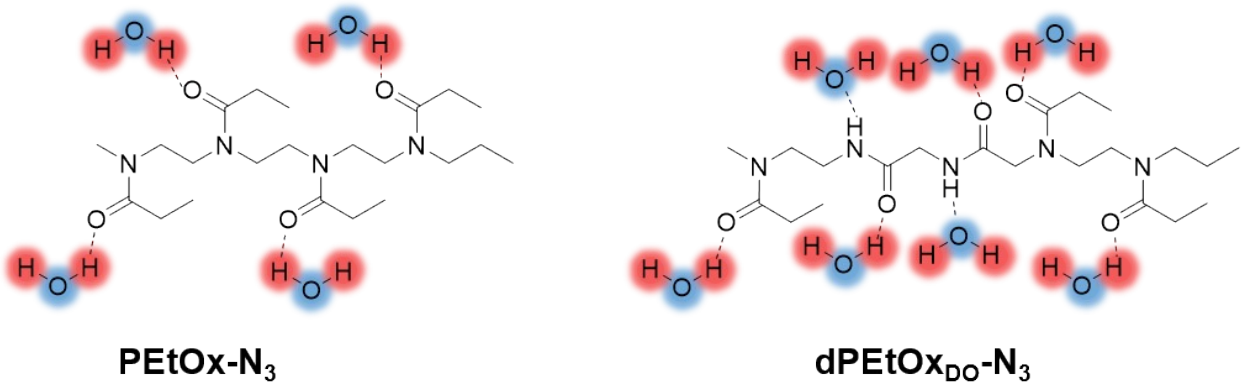

Figure SI 22: Schematic representation of possible hydrogen bond binding sites in the structures of PEtOx and dPEtOx. Hydrogen bond donating amide moieties are introduced through the glycine moieties in dPEtOx.

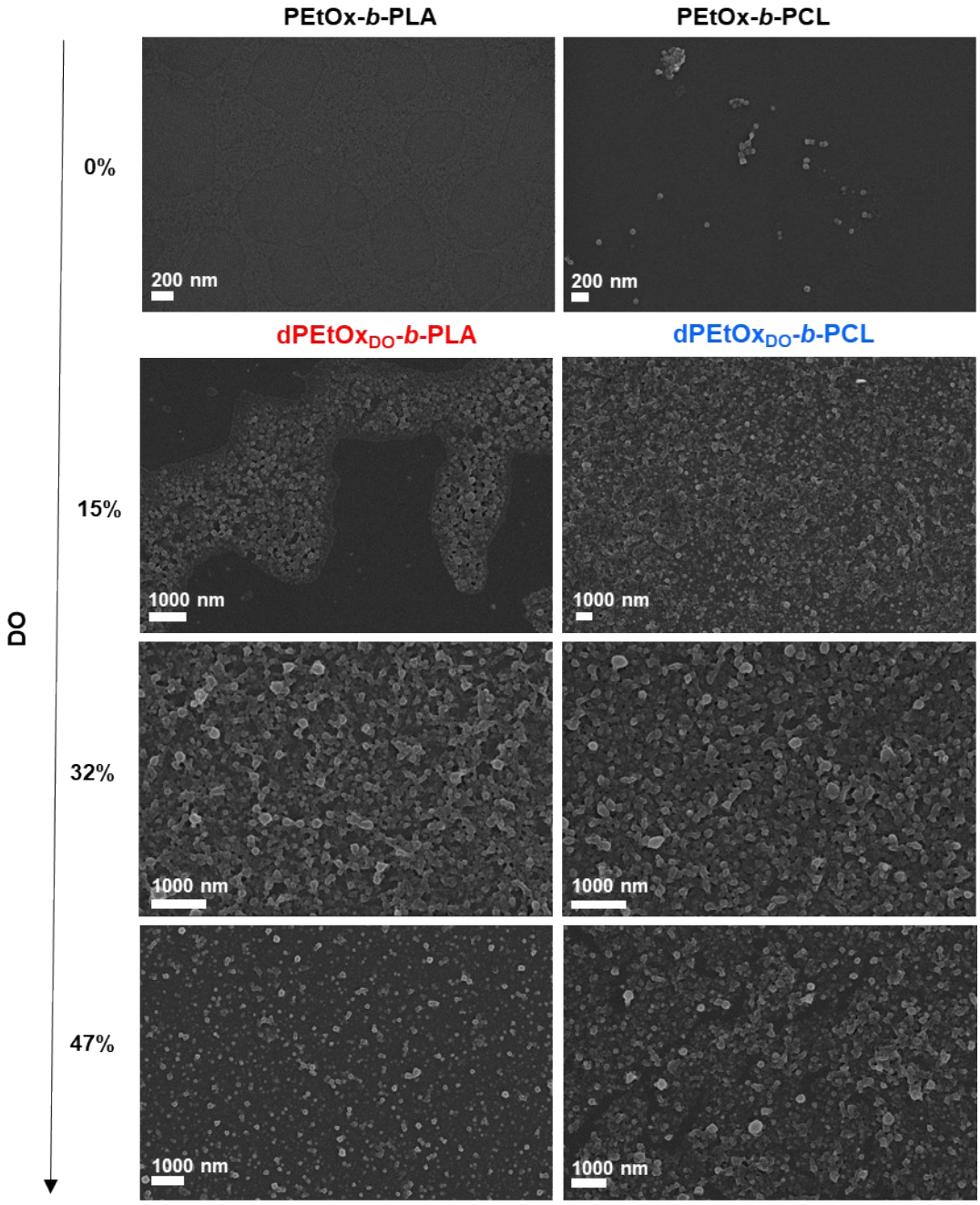

Figure SI 23: SEM images of particles formulated with 3 mg mL^{-1} initial polymer concentration.

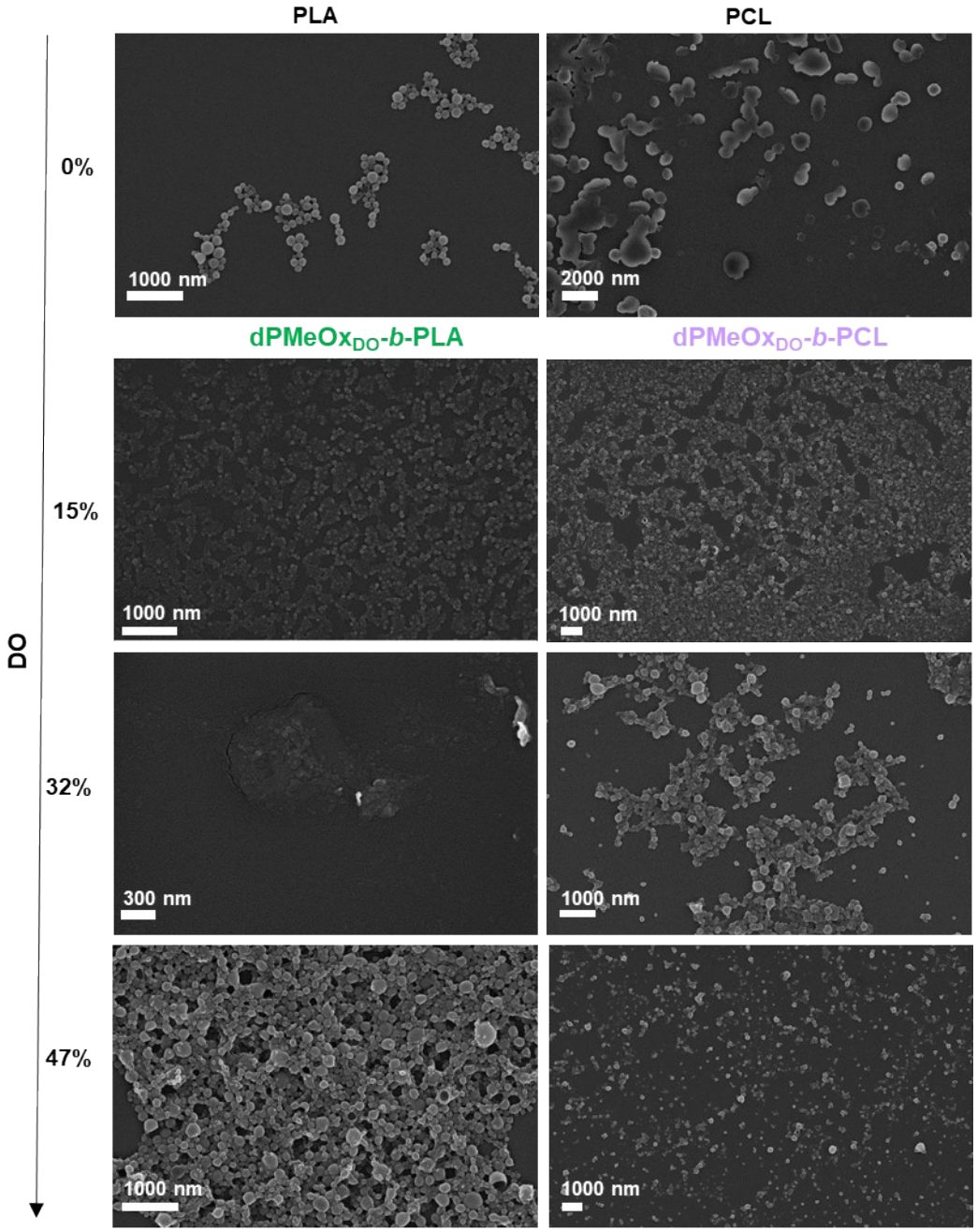

Figure SI 24: SEM images of particles formulated with 3 mg mL^{-1} initial polymer concentration.

Table SI 5: Evaluation of the particle formulation in dependency of the resulting dispersity of the size distribution. Green – successful and reliable particle formulation achieved; yellow – particle formulation possible, but the tendency of aggregation at higher concentrations; red – particle formulation critical or not successful.

P	**Polymer**	**F#**
1	BCN-PLA	
2	PEtOx-*b*-PLA	
3	dPMeOx$_{15\%}$-*b*-PLA	
4	dPEtOx$_{15\%}$-*b*-PLA	
5	dPMeOx$_{32\%}$-*b*-PLA	
6	dPEtOx$_{32\%}$-*b*-PLA	
7	dPMeOx$_{47\%}$-*b*-PLA	
8	dPEtOx$_{47\%}$-*b*-PLA	
9	BCN-PCL	
10	PEtOx-*b*-PCL	
11	dPMeOx$_{15\%}$-*b*-PCL	
12	dPEtOx$_{15\%}$-*b*-PCL	
13	dPMeOx$_{32\%}$-*b*-PCL	
14	dPEtOx$_{32\%}$-*b*-PCL	
15	dPMeOx$_{47\%}$-*b*-PCL	
16	dPEtOx$_{47\%}$-*b*-PCL	

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3. S. Osawa, T. Ishii, H. Takemoto, K. Osada and K. Kataoka, *Eur. Polym. J.*, 2017, **88**, 553–561.