

Supporting Information to

***N*-Heterocyclic Olefin-Based (Co)polymerization of a Challenging Monomer: Homopolymerization of ω -Pentadecalactone and Its Copolymers with γ -Butyrolactone, δ -Valerolactone, and ϵ -Caprolactone**

Patrick Walther and Stefan Naumann

University of Stuttgart, Institute for Polymer Chemistry, 70569 Stuttgart, Germany

E-Mail: Stefan.naumann@ipoc.uni-stuttgart.de

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Experimental

Materials and Synthesis

ϵ -Caprolactone (CL), δ -Valerolactone (VL) and γ -Butyrolactone (GBL) were stirred over CaH_2 overnight, distilled under nitrogen, degassed twice and subsequently stored under inert conditions (glove box, LabMaster, MBraun, Germany). ω -Pentadecalactone was dissolved in toluene and stirred over molecular sieves (3 Å) overnight. After exchanging the molecular sieves and additional stirring overnight, toluene was removed under reduced pressure. THF and toluene used in polymerizations were taken from a solvent purification system (MBraun, Germany) and stored inside the glove box over molecular sieves (3 Å). LiCl (Sigma Aldrich, powder, $\geq 99.99\%$ trace metals basis), MgCl_2 (Alfa Aesar, "ultra dry", 99.9%), MgI_2 (ABCR, "ultra dry", 99.996%, beads, ampouled under argon), YCl_3 (Alfa Aesar, "ultra dry", 99.99%, ampouled under argon) and ZnI_2 (Acros, "extra pure", 99.999%) were used as received and stored inside the glove box under exclusion of light.

For characterization of NHOs **1** – **3**, see published literature.¹⁻⁴ The thus received NHOs were stored inside the glove box under nitrogen at -36°C .

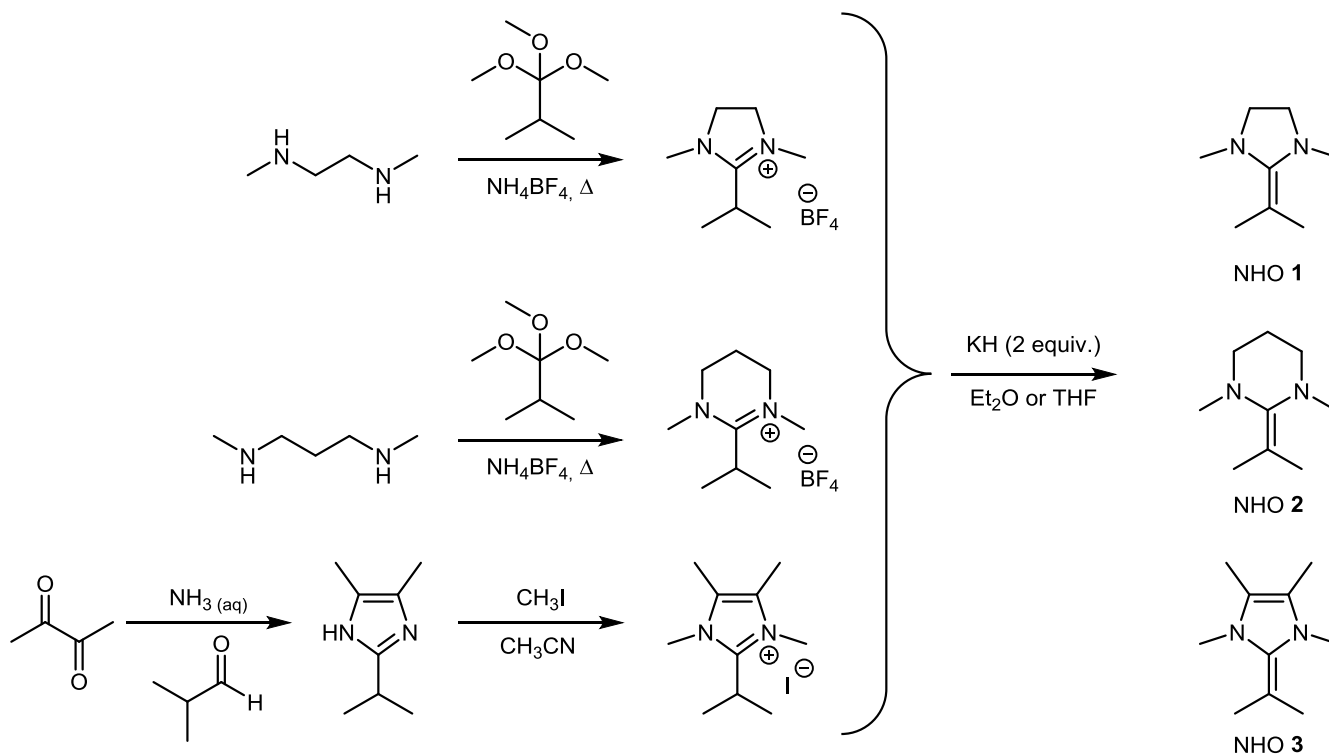


Figure S1. General procedure for the preparation of NHOs **1** – **3** used in this work.

General Polymerization Procedures

Prior to setting up the individual polymerization reactions, a 1.0 M stock solution of the corresponding monomer (ω -Pentadecalactone) in the respective solvent (THF or toluene) was prepared. Reactions at room temperature were conducted inside the glove box, whereas reactions at elevated temperatures were performed under inert atmosphere (N_2) using standard Schlenk techniques. The polymerizations were stopped by precipitation from high-boiling petroleum ether, affording a colorless precipitate, except for reactions where Lewis Acids containing iodide (MgI_2 , ZnI_2) were employed. In these cases, the precipitate exhibited off-white to yellow discoloration. Proton NMR spectroscopy was used to determine the conversion, by monitoring the $-CH_2-O-$ signal of the applied monomers (PDL: $\delta = 4.13$ ppm, CL: $\delta = 4.22$ ppm, VL: $\delta = 4.34$ ppm, GBL: $\delta = 4.31$ ppm) and resulting polymers (PPDL: $\delta = 4.08$ ppm, PGBL: $\delta = 4.07$ ppm). Heat-dried glass pipettes (110 °C, overnight) were used to draw aliquots from reactions outside the box, while applying N_2 - flow. For determination of M_n via NMR end group analysis, the CH_2 -unit of the initiator (BnOH) was used ($\delta = 5.05$ ppm, $CDCl_3$).

Homopolymerization of PDL

After providing the respective Lewis Acid (0.125 mmol) inside a suited reaction vessel, 2.5 mL of the stock solution was added with an Eppendorf syringe and stirred vigorously to afford a clear solution. Subsequently, the initiator BnOH (0.05 mmol) and the corresponding *N*-Heterocyclic Olefin (0.025 mmol) were added to result in a total molar ratio of $NHO/BnOH/M_x/PDL = 1:2:5:100$ in the reaction solution.

General Procedure for the Copolymerization Reactions

Copolymerization reactions were assembled analogously to the procedure mentioned above, to give a resulting molar ratio of $NHO/BnOH/LA/Co(1)/Co(2)$ of 1:2:5:100:100 and an initial monomer concentration (total of both lactones) of 2 mol/L. Prior to setting up the reaction, the accuracy of the stock solution was controlled using proton NMR spectroscopy. Analyzing the above mentioned triplets of both respective comonomers and resulting copolymers (PPDL-PCL: $\delta = 3.97 - 4.11$ ppm, PPDL-PVL: $\delta = 3.95 - 4.05$ ppm, PGBL-PCL: $\delta = 4.00 - 4.13$ ppm, PGBL-PVL: $\delta = 3.99 - 4.10$ ppm), the conversion was followed by 1H NMR spectroscopy. Isolation of the copolymers was realized by precipitation from high-boiling petroleum ether to yield colorless to yellowish (MgI_2 and ZnI_2) solids for copolymers incorporating PPDL, or colorless, oily liquids when the copolymers contained GBL-derived repeating units. The molecular weight of the isolated and dried copolymers was investigated using GPC ($CHCl_3$).

Characterization and Analysis

$^1H/^{13}C$ NMR spectra were recorded on a *Bruker Avance III 400* spectrometer, with the chemical shifts being reported relative to reference peaks of the applied deuterated solvents ($CDCl_3$: $\delta = 7.26/77.16$ ppm for proton and carbon spectra, respectively). GPC ($CHCl_3$, 40 °C) was used to determine the molecular weight of synthesized (co)polymers, calibrated with a polystyrene standard. A chromatographic assembly comprising a *PSS SDV 5 μm 8*50mm* guard column, three *PSS SDV 100 000 Å 5 μm 8*50mm* columns and an *Agilent 1200 Series G1362A* detector (RI) was used. The concentration of the prepared samples amounted to 2.5 mg/mL, and a flow-rate of 1 mL/min was applied during the analyses. For Differential Scanning Calorimetry (DSC), a *Perkin Elmer DSC 4000* was used (scanning rate 5 K/min, 20 mL/min nitrogen flow, temperature range 0 °C to 100 °C and 30 °C to 130 °C, respectively). Thermograms were analyzed using the second heating/cooling cycle.

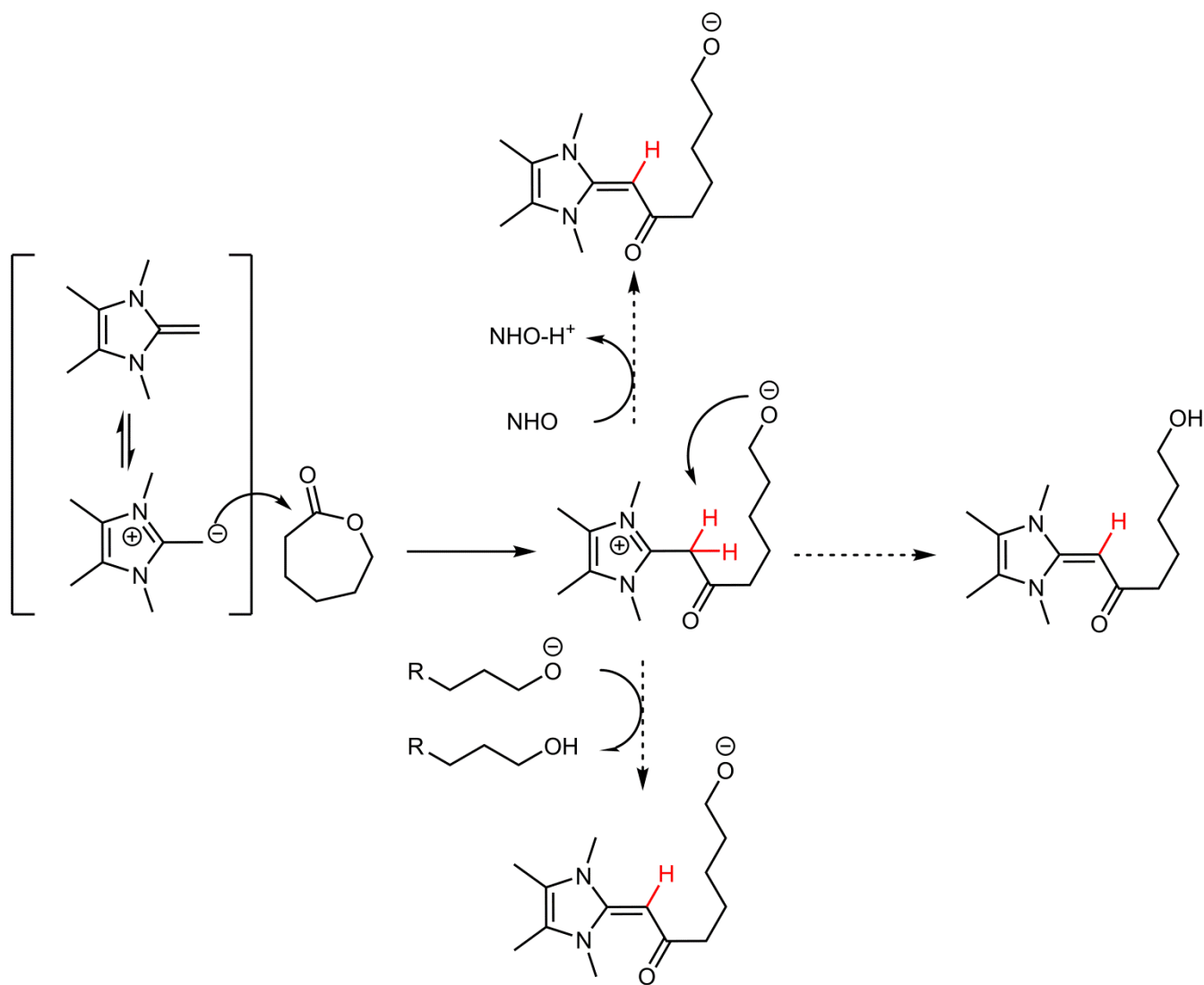


Figure S2. Schematic representation of enamine formation (= deoxy Breslow intermediate) in lactone polymerization using =CH₂-bearing NHOs. These compounds can directly ring-open the monomer, forming a zwitterionic intermediate. This structure displays acidified protons (red). Supposedly, a proton transfer can occur with several basic species present in the polymerization setup, including deprotonation by growing anionic chain ends (intra- and intermolecular) or by free NHOs. In either case, one equivalent of catalyst is deactivated. This side reaction cannot occur with substituted NHOs (=CR₂).

Control Reactions (no dual catalysis)

Table S1. Control reactions for PDL polymerization in the absence of Lewis acid.

NHO	Lewis Acid (MX _n)	NHO/BnOH/MX _n /PDL	Time [min]	Conversion ^a [%]
1	-	1:2:0:100	240	0
1	-	1:0:0:100	240	0
2	-	1:2:0:100	240	0
2	-	1:0:0:100	240	0
3	-	1:2:0:100	240	40 ^b
3	-	1:0:0:100	240	0

Polymerization conditions: 110 °C in toluene, [M]₀ = 1.0 M. ^aMonomer conversion determined *via* ¹H-NMR spectroscopy. ^bmolecular weight of the polymer determined *via* GPC (CHCl₃) to be 15000 g/mol, with $\bar{D}_M = 1.52$.

Homopolymerization of PDL

Table S2. Homopolymerization of PDL using NHO/metal halide LPs (THF).

NHO	Lewis Acid	Time [min]	Conversion ^a [%]	M_n^b [g·mol ⁻¹]	$\bar{D}_M^b$
2	MgI ₂	60	89	34200	1.35
		120	94	31000	1.61
		240	96	24000	2.0
2	ZnI ₂	60	10	1800	1.52
		120	17	2200	1.95
		240	28	8200	1.43
2	YCl ₃	60	13	2500	1.26
		120	19	4900	1.23
		240	33	8700	2.2

Polymerization conditions: 100 °C in THF, [M]₀ = 1.0 M. ^aMonomer conversion determined *via* ¹H-NMR spectroscopy. ^bmolecular weight determined *via* GPC (CHCl₃).

Table S3. Homopolymerization of PDL using NHO/metal halide LPs (toluene).

NHO	Lewis Acid	Time [min]	Conversion ^a [%]	M_n^b [g·mol ⁻¹]	D_M^b
1	LiCl	240	6	-	-
	MgCl ₂	15	26	7400	1.45
		60	84	26200	1.58
		120	94	25200	1.76
		240	94	30000	1.49
	MgI ₂	15	77	19200	1.62
		60	95	22900	1.64
		120	96	20700	1.64
		240	96	17100	1.73
	ZnI ₂	15	2	-	-
		60	13	2300	1.27
		120	20	4000	1.56
		240	35	4500	2.4
	YCl ₃	15	12	2900	1.36
		60	49	13300	1.51
		120	72	18800	1.61
		240	86	20500	2.2
2	LiCl	240	2	-	-
	MgCl ₂	15	37	6600	1.49
		60	86	12400	2.0
		120	92	13800	2.0
		240	95	14200	2.1
	MgI ₂	15	80	11600	1.73
		60	92	10700	2.0
		120	93	12600	1.60
		240	97	9600	1.91
	ZnI ₂	120	15	3600	1.05
		240	19	4600	1.26

2	YCl ₃	15	14	3000	(1.22)
		60	47	6700	(1.66)
		120	68	10000	1.69
		240	85	12200	1.78
3	LiCl	15	35	10500	1.51
		60	72	20600	1.51
		120	83	24300	1.54
		240	86	26600	1.52
	MgCl ₂	15	14	5600	1.46
		60	42	14500	1.57
		120	60	22100	1.48
		240	75	26500	1.49
	MgI ₂	15	57	17000	1.47
		60	87	21500	1.60
		120	94	22100	1.65
		240	95	20900	1.58
	ZnI ₂	240	14	3700	1.61
	YCl ₃	60	32	7900	1.68
		120	55	11700	1.95
		240	74	18200	1.61

Polymerization conditions: 110 °C in toluene, [M]₀ = 1.0 M. ^aMonomer conversion determined *via* ¹H-NMR spectroscopy. ^bmolecular weight determined *via* GPC (CHCl₃).

Correlation of M_n and conversion

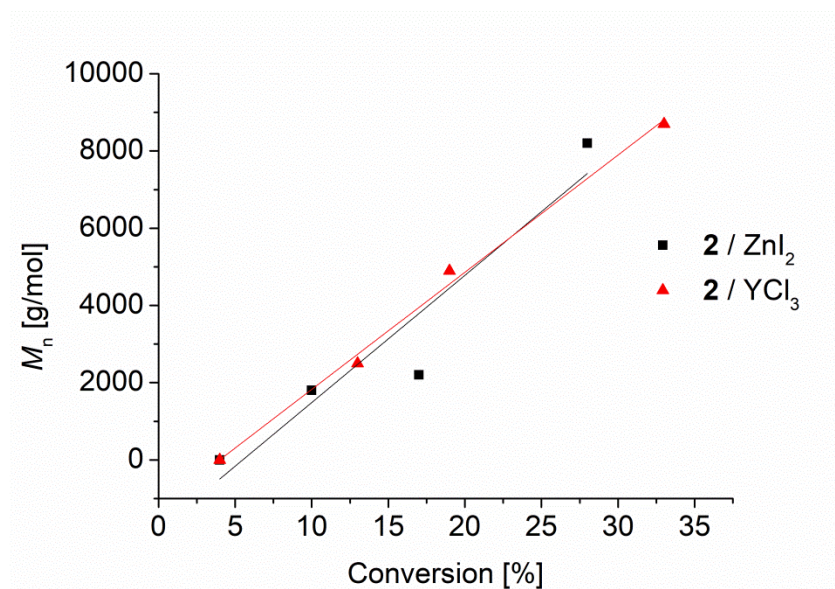


Figure S3. Correlation of molecular weight (determined by GPC (CHCl_3)) vs. conversion for PDL homopolymerization using **2** with ZnI_2 and YCl_3 . Conditions: **2**/BnOH/ MX_n /PDL = 1:2:5:100, $[\text{M}]_0 = 1.0$ mol/L, toluene, $T = 110$ °C.

Correlation of M_n (GPC) and M_n (NMR) in PDL homopolymerization

Table S4. Comparison of molecular weights determined via GPC (CHCl_3 , PS, data from Table S2) and end group analysis (^1H NMR spectroscopy).

NHO	MX_n	time [min]	Conversion ^{a)} [%]	$M_{n,\text{GPC}}$ ^{b)} [g/mol]	$M_{n,\text{NMR}}$ ^{c)} [g/mol]
1	LiCl	240	6	2900	1575
1	MgCl_2	15	26	7400	6300
		60	84	26200	21150
		120	94	25200	24525
		240	94	30000	24975
1	MgI_2	15	77	19200	18675
		60	95	22900	21150
		120	96	20700	24300
		240	96	17100	31725
1	ZnI_2	60	13	2300	2700
		120	20	4000	4950
1	YCl_3	15	12	2900	3150
		60	49	13300	12150
		120	72	18800	17775
		240	86	20500	23175
2	MgCl_2	15	37	6600	7650
		60	86	12400	17550
		120	92	13800	17550
2	MgI_2	60	92	10700	9900
2	ZnI_2	60	5	2200	1575
		120	15	3600	2250
		240	22	4600	5400
2	YCl_3	15	14	3000	3600
		60	47	6700	10350
3	LiCl	15	35	10500	9900
		60	72	20600	19800
		120	83	24300	21600

		240	86	26600	24300
3	MgCl ₂	15	14	5600	4050
3	MgCl ₂	60	42	14500	10125
3	MgI ₂	15	57	17000	13725
		60	87	21500	23175
		120	94	22100	30375
		240	95	20900	25425
3	ZnI ₂	240	14	3700	4050
3	YCl ₃	60	32	7900	8550
		120	55	11700	13275
		240	74	18200	18675

^{a)} conversion determined *via* ¹H NMR analysis (CDCl₃); ^{b)} molecular weight determined *via* GPC (CHCl₃, PS); ^{c)} molecular weight determined *via* ¹H NMR endgroup analysis (multiplied by a correctional factor of 2.25).

Copolymerization reactions

Copolymerization of PDL/VL

Table S5. Copolymerization of PDL/VL using various NHO/Lewis Acid combinations.^a

no.	NHO	Lewis Acid	time [min]	conv. ^b [%]	M_n^c [g·mol ⁻¹]	$\bar{D}_M^c$
1	2	LiCl	240	41	3800	1.99
2	2	MgI ₂	240	38	6100	1.79
3	2	ZnI ₂	240	36	10000	1.35
4	2	YCl ₃	240	78	15900	1.87

^aConditions: molar ratio of NHO/BnOH/M_x/PDL/VL = 1:2:5:100:100, [M]_{0,total} = 2.0 M in toluene, 110 °C. ^bMonomer conversion determined *via* NMR spectroscopy. ^cDetermined *via* GPC analysis (CHCl₃).

Copolymerization of PDL/GBL

Table S6. Copolymerization of PDL with GBL using **2** and various Lewis Acids.^a

no.	Lewis Acid	time [min]	conv. ^b [%]	M_n^c [g·mol ⁻¹]	D_M^c
1	LiCl	240	18	6900	1.43
		20 h	19	7600	1.43
		24 h	19	7900	1.45
2	MgCl ₂	240	10	2700	1.12
		24 h	11	4100	1.28
		27 h	21	5000	1.31
3	ZnI ₂	240	11	4800	1.27
		20 h	25	13900	1.52
		24 h	27	14500	1.68
		48 h	35	14600	1.80
4	YCl ₃	15	5	-	-
		60	10	2000	1.45
		120	11	3600	1.55
		240	17	7100	1.59
		86 h	58	20900	1.79

^aConditions: molar ratio of NHO/BnOH/M_x/PDL/VL = 1:2:5:100:100, [M]_{o,total} = 2.0 M in THF, 100 °C. ^bMonomer conversion determined *via* NMR spectroscopy. ^cDetermined *via* GPC analysis (CHCl₃).

Representative ^1H -NMR analysis of a copolymer

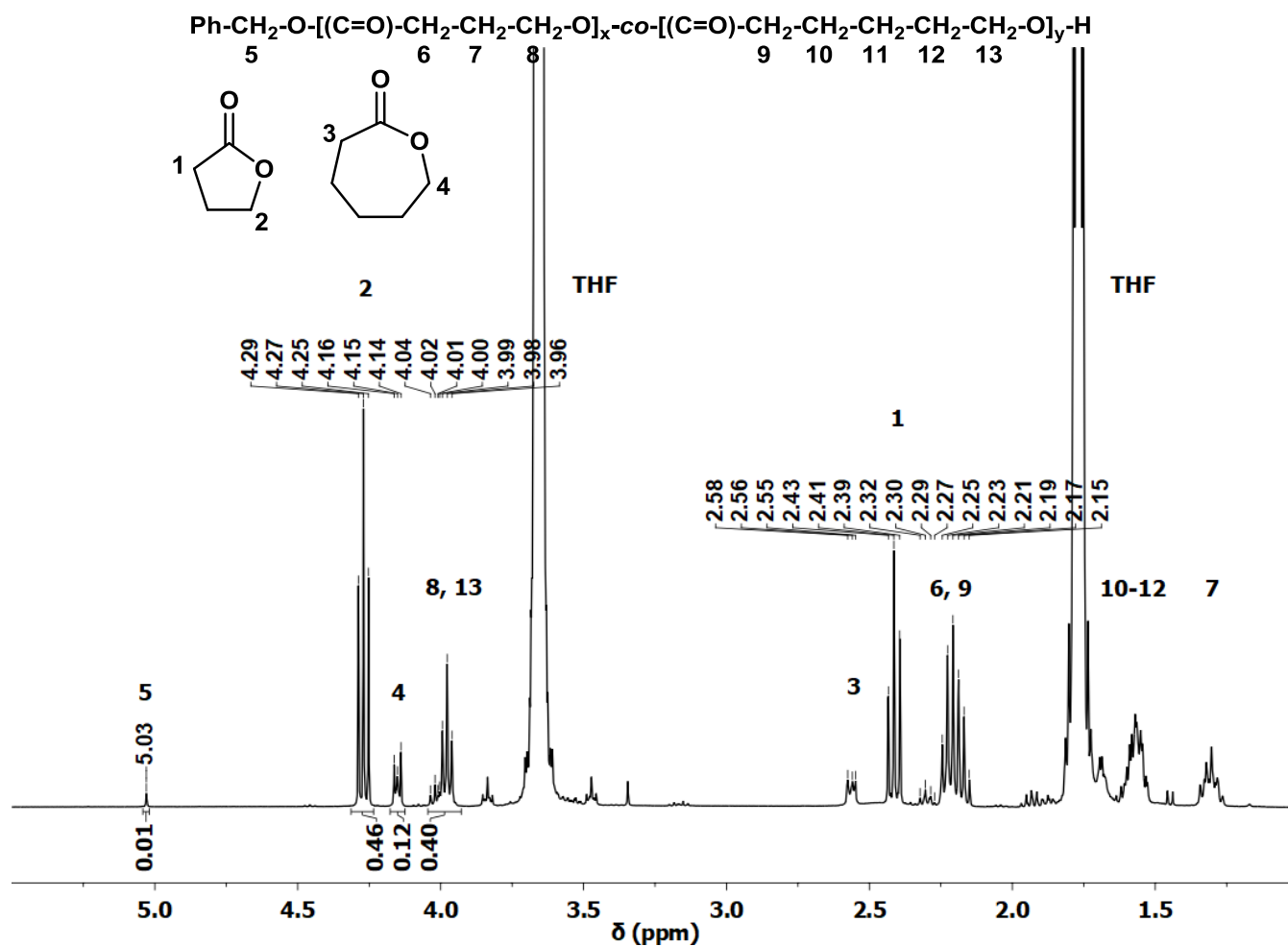


Figure S4. ^1H -NMR spectrum (CDCl_3 , 400 MHz) of an aliquot drawn from a copolymerization using **2**/ MgI_2 . Conditions: **2**/ BnOH / MgI_2 / GBL / CL = 1:2:5:100:100, 100 $^\circ\text{C}$, THF, $T = \text{r.t.}$, $[\text{M}]_{0,\text{total}} = 2.0 \text{ mol/L}$, $t = 2 \text{ h}$, 41 % conversion. In order to fully preclude evaporation of GBL, the sample was not dried *in vacuo* prior to ^1H NMR analysis.

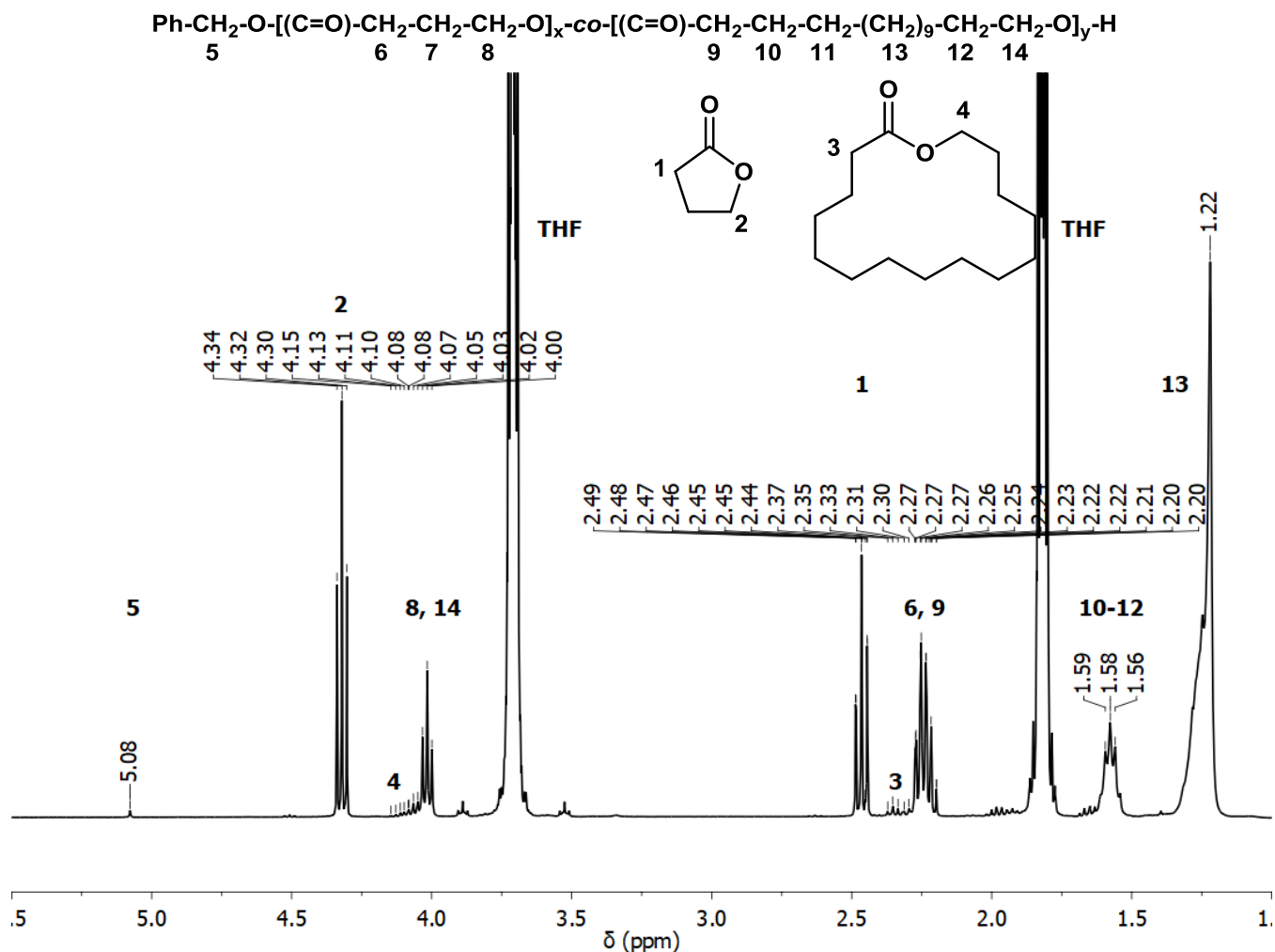


Figure S5. ^1H -NMR spectrum (CDCl_3 , 400 MHz) of an aliquot drawn from a copolymerization using **2**/ YCl_3 . Conditions: **2**/ BnOH / YCl_3 / PDL / GBL = 1:2:5:100:100, toluene, $[\text{M}]_{\text{o, total}} = 2.0 \text{ mol/L}$, 58 % conversion, after 8 h at 50 °C and 16h at 110 °C. In order to fully preclude evaporation of GBL, the sample was not dried *in vacuo* prior to ^1H NMR analysis. ^1H -NMR (400 MHz, CDCl_3) δ = 5.08 (Ph- $\underline{\text{CH}_2}$ -O-), 4.32 (t, $J = 7.1 \text{ Hz}$, GBL- $\underline{\text{CH}_2}$ -O-(C=O)-), 4.15 – 4.00 (m, Poly- $\underline{\text{CH}_2}$ -O-), 2.47 (t, $J = 8.2 \text{ Hz}$, GBL- $\underline{\text{CH}_2}$ -(C=O)-), 2.38 – 2.16 (m, Poly- $\underline{\text{CH}_2}$ -(C=O)-), 1.59 – 1.56 (m), 1.22 (m).ppm.

Copolymerization of GBL with CL and VL

Table S7. Full data set of GBL copolymerization with CL and VL, using **2** in combination with various Lewis acids.

no.	Comonomer (Co)	Lewis Acid	time [min]	conv. ^b [%]	M_n^c [g·mol ⁻¹]	$\bar{D}_M^c$	Dyad sequence distribution [%]			
							Co-GBL	Co-Co	GBL-Co	GBL-GBL
1	CL	LiCl	120	52	6900	1.49	11	74	11	4
2	CL	MgCl ₂	120	36	4100	1.09	16	68	16	-
3	CL	MgI ₂	120	42	5900	1.12	11	78	11	-
4	CL	ZnI ₂	120	55	8000	1.13	10	80	10	-
5	CL	YCl ₃	120	61	4600	1.18	15	70	15	-
6	VL	LiCl	120	24	2200	2.2	9	82	9	-
7	VL	MgCl ₂	120	16	2700	1.13	8	84	8	-
8	VL	MgI ₂	120	37	5300	1.14	6	88	6	-
9	VL	ZnI ₂	120	9	4900	1.22	4	91	4	1
10	VL	YCl ₃	120	37	3900	1.24	12	76	12	-
11 ^d	CL	LiCl	24 h	66	6600	2.4	22	56	22	-
12 ^d	CL	MgCl ₂	24 h	33	600	1.34	-	-	-	-
13 ^d	CL	ZnI ₂	24 h	39	4800	1.06	10	73	10	7
14 ^d	CL	YCl ₃	24 h	57	1200	2.0	15	70	15	-
15 ^d	CL	-	24 h	3	-	-	-	-	-	-
16 ^d	VL	LiCl	24 h	46	5400	1.45	9	82	9	-
17 ^d	VL	MgCl ₂	24 h	24	2000	1.11	8	84	8	-
18 ^d	VL	ZnI ₂	24 h	49	5200	1.09	5	90	5	-
19 ^d	VL	YCl ₃	24 h	42	800	1.68	-	-	-	-
20 ^d	VL	-	24 h	6	-	-	-	-	-	-

^aConditions: molar ratio of NHO/BnOH/M_x/GBL/Co = 1:2:5:100:100 [M]_{o,total} = 2.0 M in THF, r.t. ^bMonomer conversion determined *via* NMR spectroscopy. ^cDetermined *via* GPC analysis (CHCl₃). ^dT = -36°C.

Representative GPC traces resulting from GBL-CL/VL copolymers

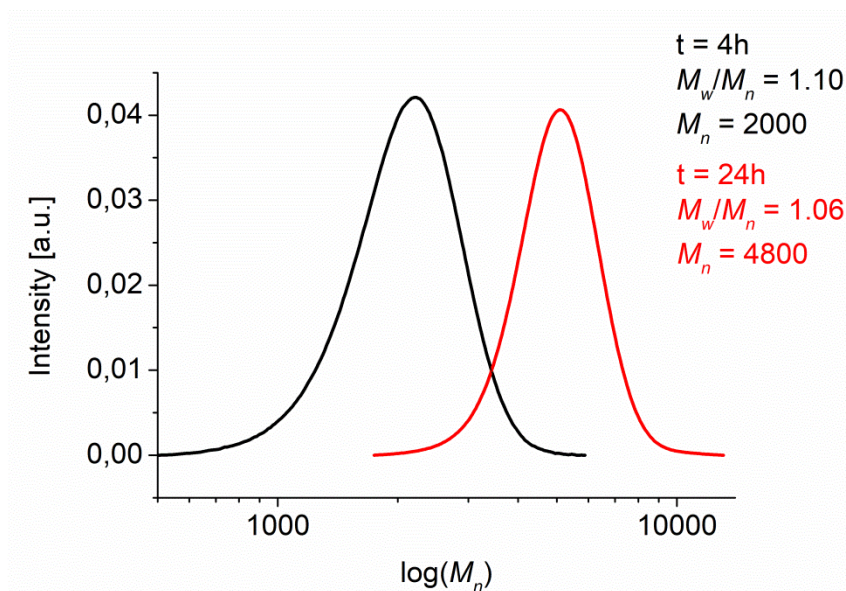


Figure S6. GPC trace received from a GBL/CL copolymer, synthesized *via* application of $\mathbf{2}/\text{ZnI}_2$ after 4 h and 24 h. $\text{NHO}/\text{BnOH}/\text{MX}_n/\text{GBL}/\text{CL} = 1:2:5:100:100$, $[\text{M}]_{\text{o, total}} = 2.0 \text{ mol/L}$, THF, $T = -36^\circ\text{C}$.

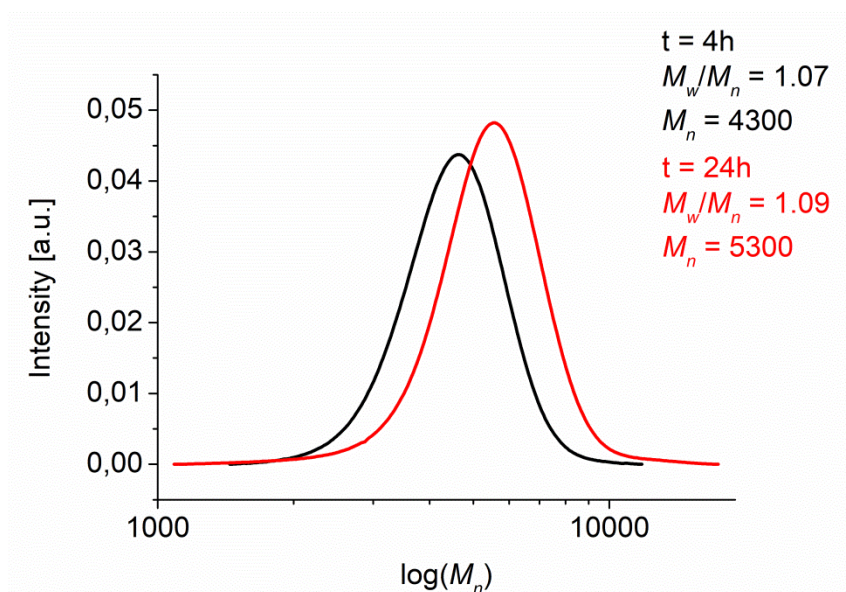


Figure S7. GPC trace received from a GBL/VL copolymer, synthesized *via* application of $\mathbf{2}/\text{ZnI}_2$ after 4 h and 24 h. $\text{NHO}/\text{BnOH}/\text{MX}_n/\text{GBL}/\text{VL} = 1:2:5:100:100$, $[\text{M}]_{\text{o, total}} = 2.0 \text{ mol/L}$, THF, $T = -36^\circ\text{C}$.

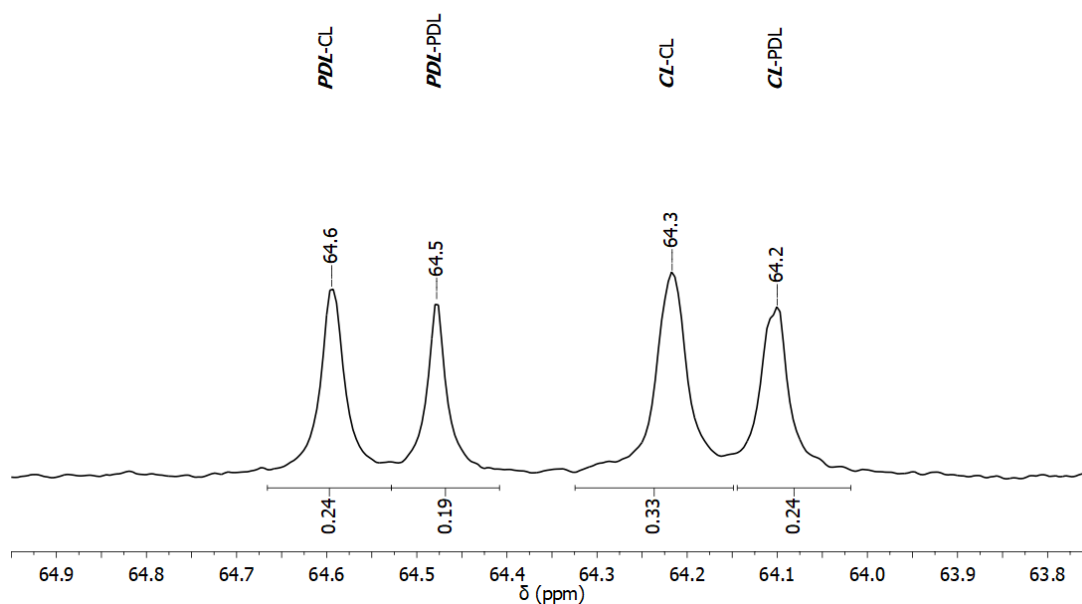


Figure S8. ¹³C NMR spectroscopy (CDCl₃, 300 K, O-CH₂ region) with dyad sequence analysis of a PDL/CL copolymer resulting from application 2/LiCl after 2 h at 100 °C.

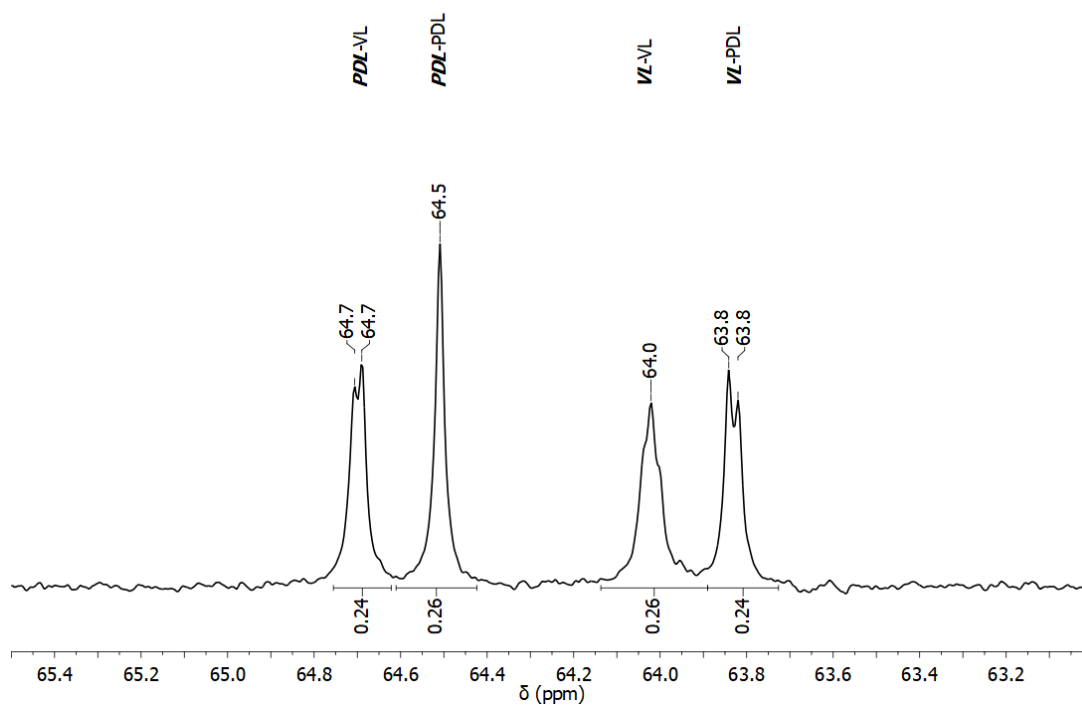


Figure S9. ¹³C NMR spectroscopy (CDCl₃, 300 K, O-CH₂ region) with dyad sequence analysis of a PDL/VL copolymer resulting from application 2/YCl₃ after 24 h at 150 °C.

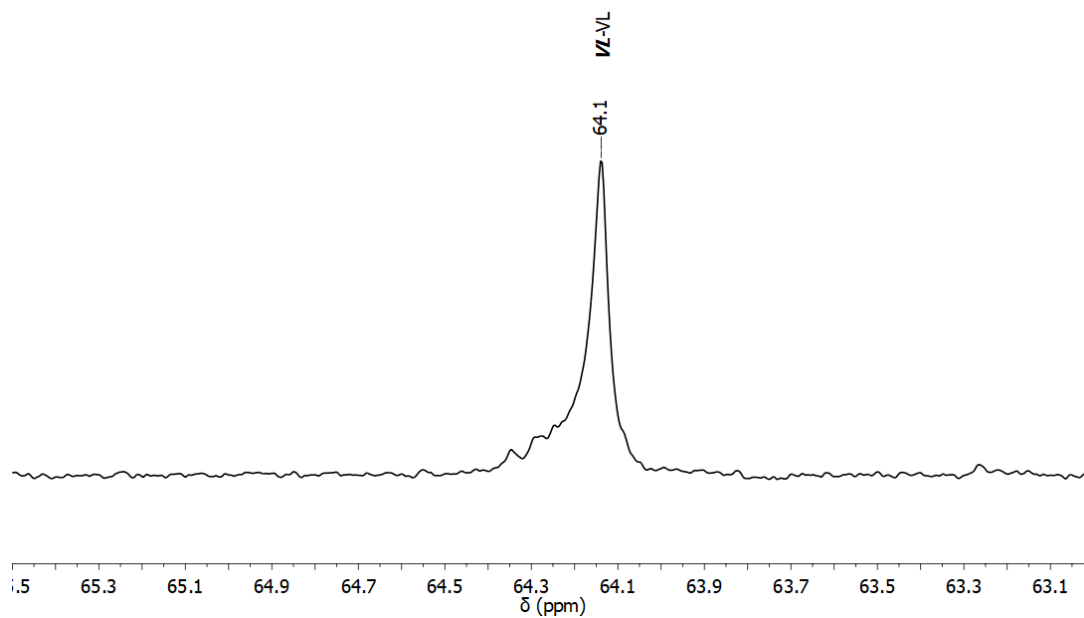


Figure S10. ^{13}C NMR spectroscopy (CDCl_3 , 300 K, $\text{O}-\underline{\text{C}}\text{H}_2$ region) with dyad sequence analysis of a PDL/VL copolymer resulting from application **2**/ ZnI_2 after 8 h at 50 $^\circ\text{C}$.

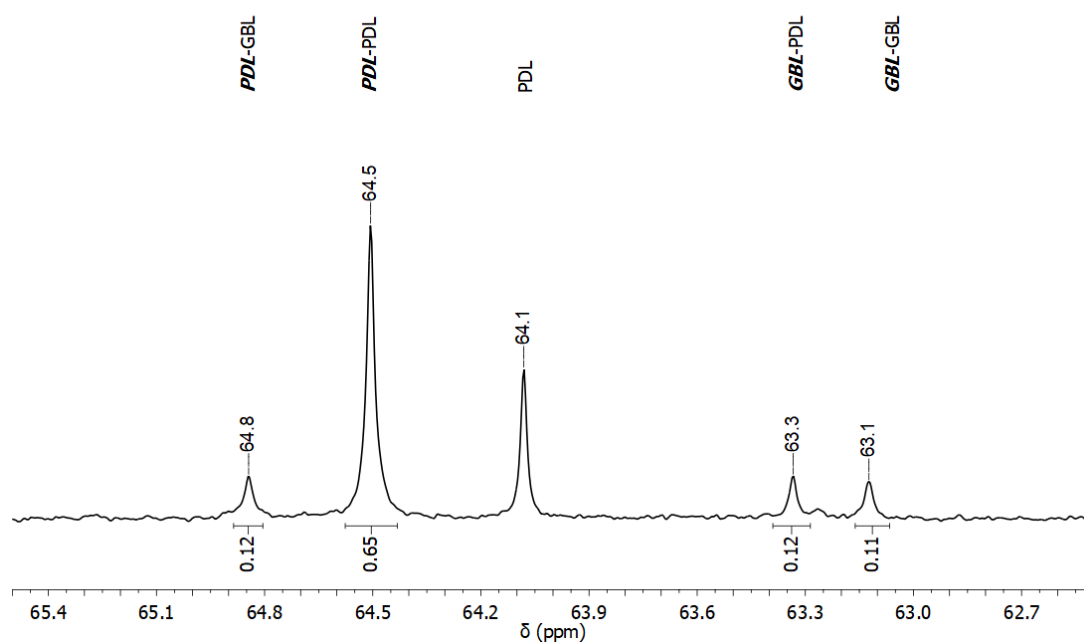


Figure S11. ^{13}C NMR spectroscopy (CDCl_3 , 300 K, $\text{O}-\underline{\text{C}}\text{H}_2$ region) with dyad sequence analysis of a PDL/GBL copolymer resulting from application **2**/ YCl_3 after 24 h at 100 $^\circ\text{C}$.

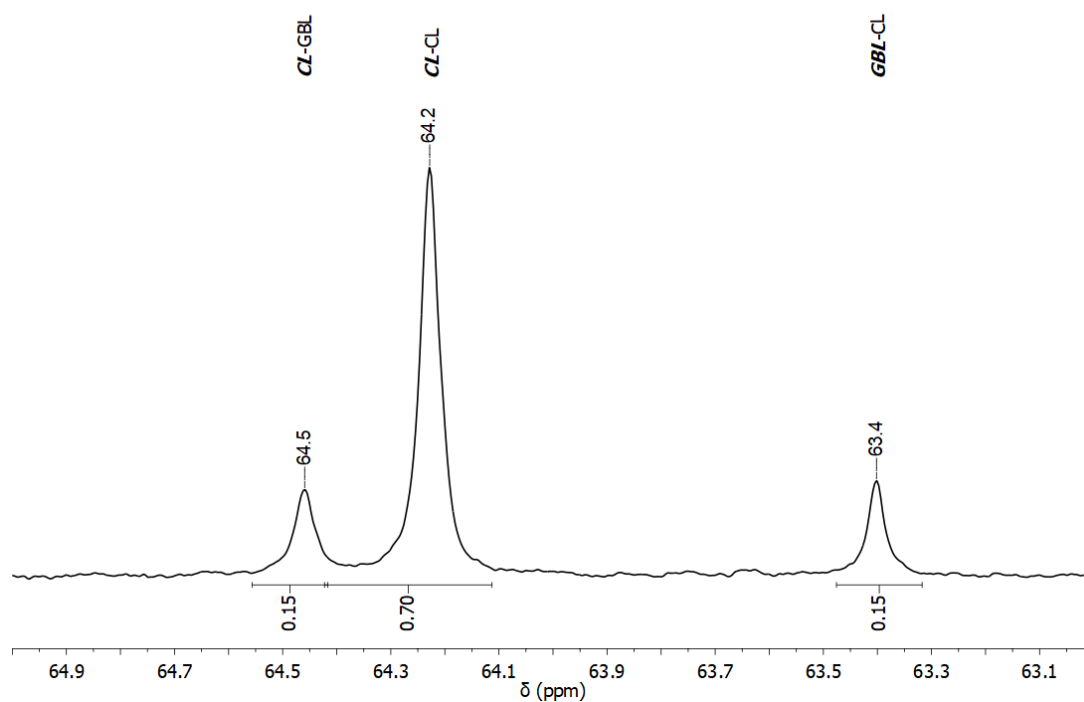


Figure S12. ^{13}C NMR spectroscopy (CDCl_3 , 300 K, $\text{O}-\text{CH}_2$ region) with dyad sequence analysis of a GBL/CL copolymer resulting from application 2/ YCl_3 after 2 h at room temperature.

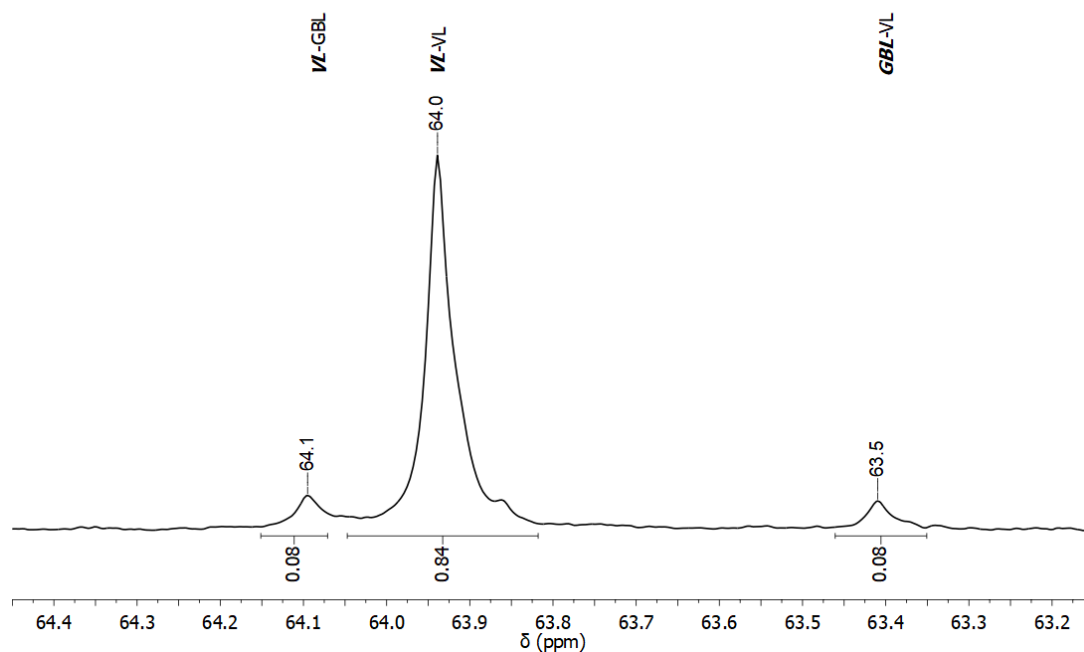


Figure S13. ^{13}C NMR spectroscopy (CDCl_3 , 300 K, $\text{O}-\text{CH}_2$ region) with dyad sequence analysis of a GBL/VL copolymer resulting from application 2/ LiCl after 2 h at room temperature.

DSC analysis of synthesized copolymers

Table S8. Melting points of copolymers determined *via* DSC analyses (heat rate = 5 K/min, purge gas flow (N₂) = 20 mL/min). For more details, see correlated tables.

Table in paper	Entry	NHO/M _x	Polymerization time	(Co)monomers		<i>T_m</i> [°C]
			[min]			
1	6	1/MgCl ₂	240	PDL	-	93
2	1	2/LiCl	240	PDL	CL	72
2	2	2/MgCl ₂	240	PDL	CL	70
2	3	2/MgI ₂	240	PDL	CL	74
2	4	2/ZnI ₂	240	PDL	CL	53
2	5	2/YCl ₃	480	PDL	CL	80
3	1	2/MgI ₂	240	PDL	VL	39
3	2	2/MgI ₂	24 h	PDL	VL	59
3	3	2/ZnI ₂	240	PDL	VL	29/41
3	4	2/ZnI ₂	24 h	PDL	VL	30
3	5	2/YCl ₃	240	PDL	VL	38
3	6	2/YCl ₃	24 h	PDL	VL	72
4	1	2/LiCl	24 h	PDL	GBL	79
4	2	2/MgCl ₂	27 h	PDL	GBL	84
4	3	2/ZnI ₂	48 h	PDL	GBL	85
4	4	2/YCl ₃	86 h	PDL	GBL	91
4	5	2/LiCl	63	PDL	GBL	86
4	6	2/LiCl	24	PDL	GBL	79
5	4	2/ZnI ₂	120	GBL	CL	42
5	5	2/YCl ₃	120	GBL	CL	35
5	8	2/MgI ₂	120	GBL	VL	39
5	9	2/YCl ₃	120	GBL	VL	31
5	10	2/LiCl	24 h	GBL	CL	34
5	11	2/ZnI ₂	24 h	GBL	CL	39
5	13	2/LiCl	24 h	GBL	VL	40
5	15	2/ZnI ₂	24 h	GBL	VL	45

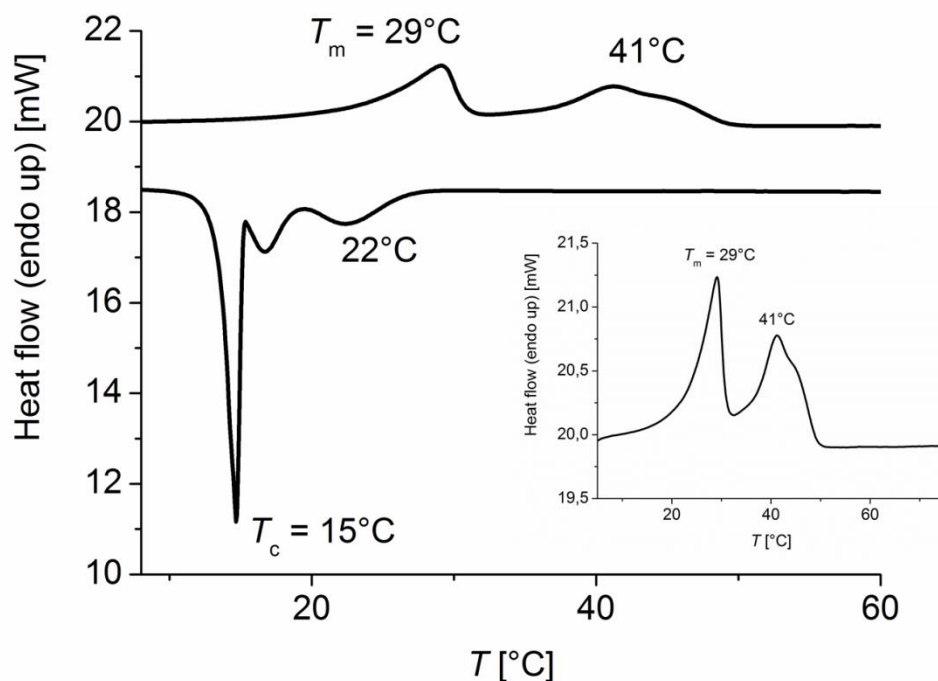


Figure S14. DSC investigation (5 K/min, second cycle) of copolymer derived from PDL and VL using $\mathbf{z}/\text{MgI}_2$ (NHO/BnOH/ M_x /PDL/VL = 1:2:5:100:100, 480 min, 50°C, toluene).

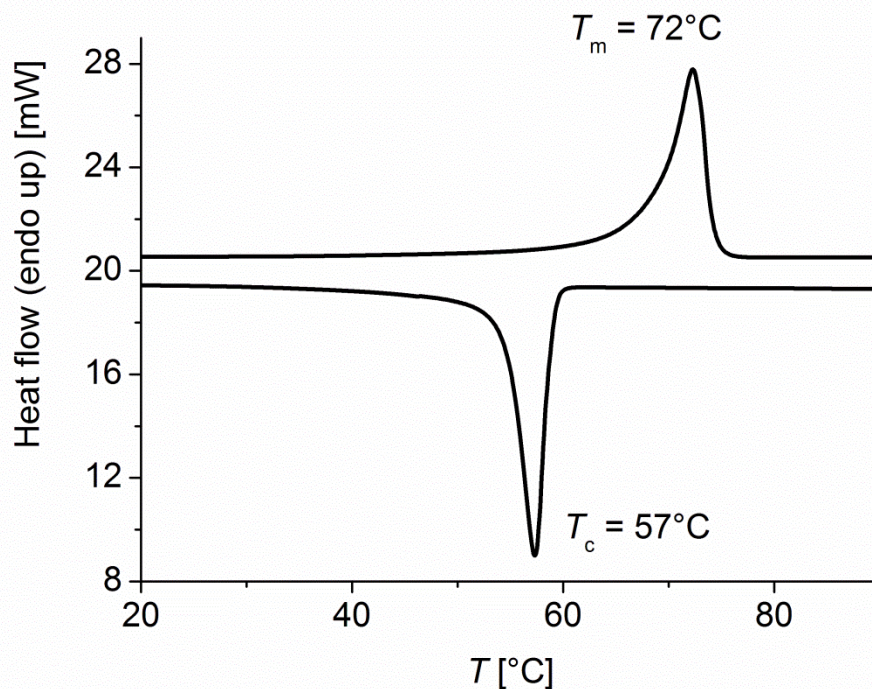


Figure S15. DSC investigation (5 K/min, second cycle) of copolymer derived from PDL and VL using $\mathbf{z}/\text{YCl}_3$ (NHO/BnOH/ M_x /PDL/VL = 1:2:5:100:100, 24 h, 110°C, toluene).

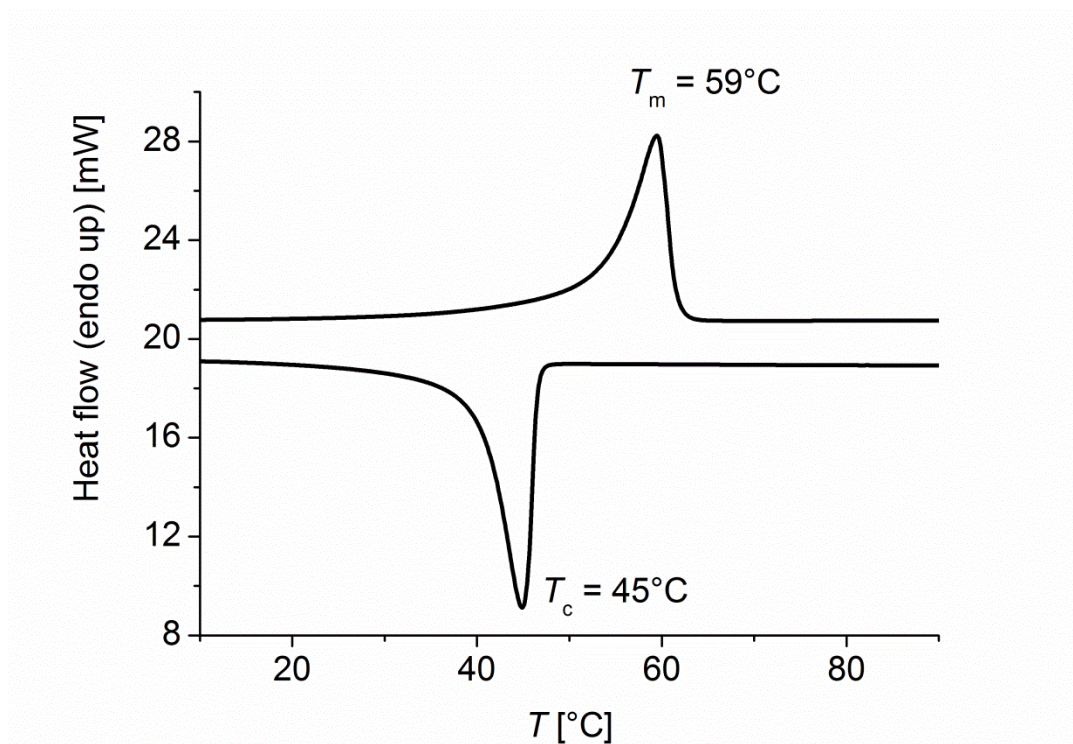


Figure S16. DSC investigation (5 K/min, second cycle) of copolymer derived from PDL and VL using $\mathbf{2}/\text{ZnI}_2$ (NHO/BnOH/ M_x /PDL/VL = 1:2:5:100:100, 24 h, 110°C, toluene).

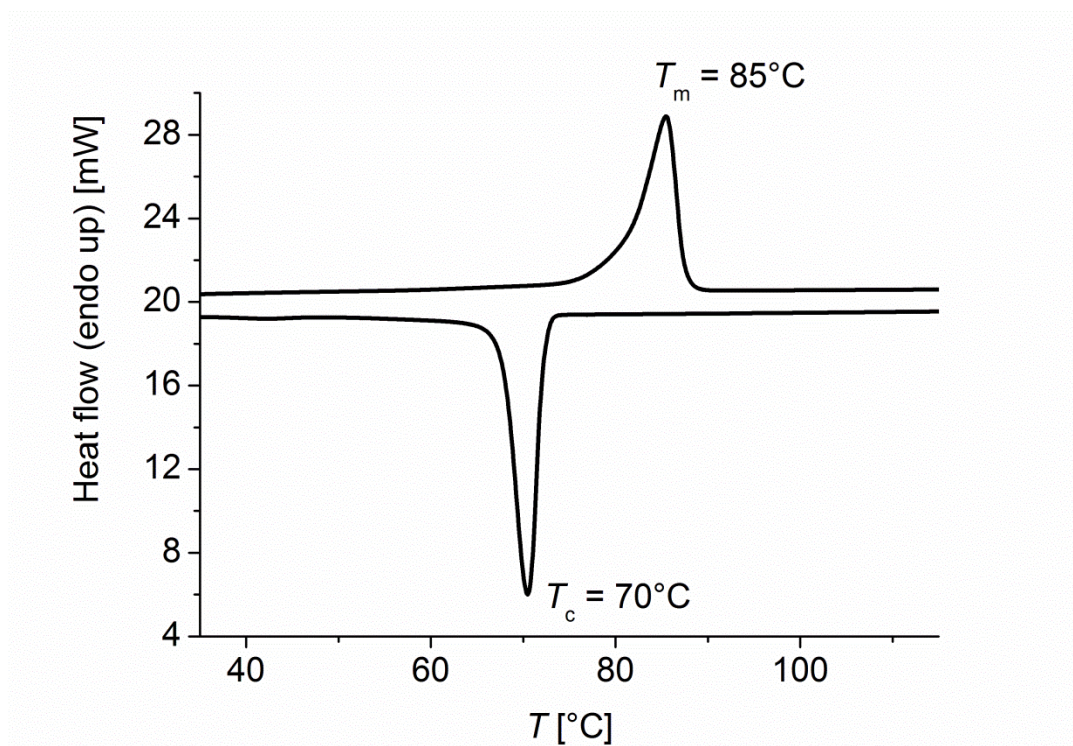


Figure S17. DSC investigation (5 K/min, second cycle) of copolymer derived from PDL and GBL using $\mathbf{2}/\text{ZnI}_2$ (NHO/BnOH/ M_x /PDL/GBL = 1:2:5:100:100, 48 h, 100°C, THF).

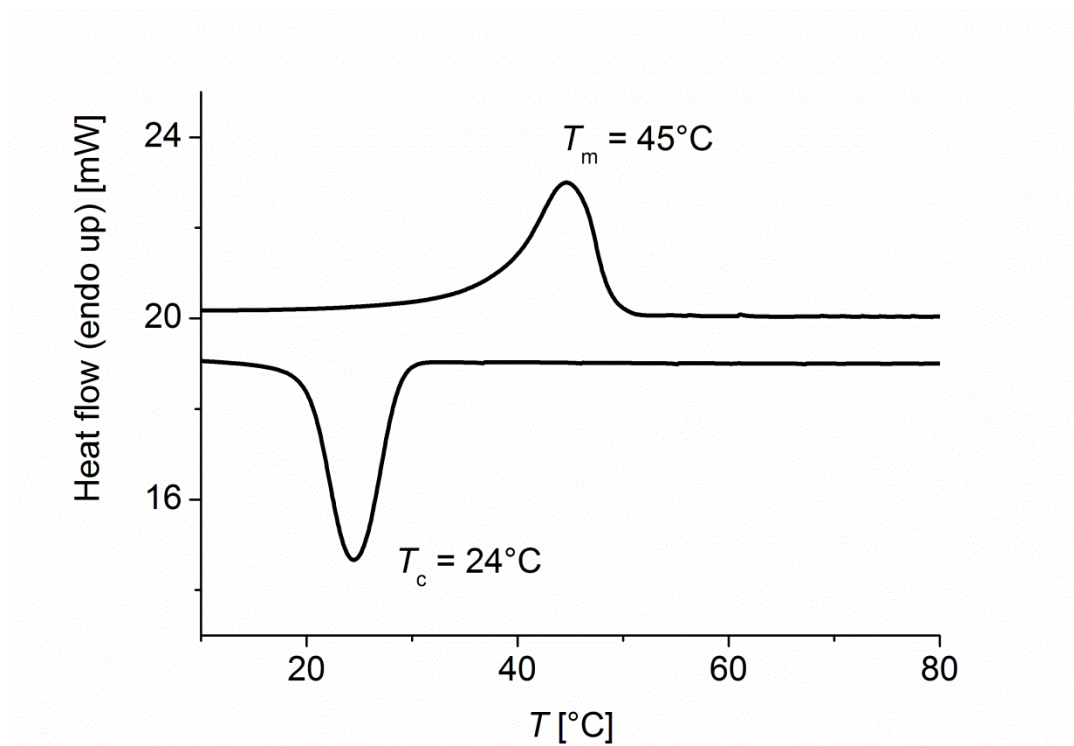


Figure S18. DSC investigation (5 K/min, second cycle) of copolymer derived from GBL and VL using $\mathbf{2}/\text{ZnI}_2$ (NHO/BnOH/ M_x /GBL/VL = 1:2:5:100:100, 24 h, -36°C , THF).

Complexation experiments analyzed via ^1H -NMR spectroscopy

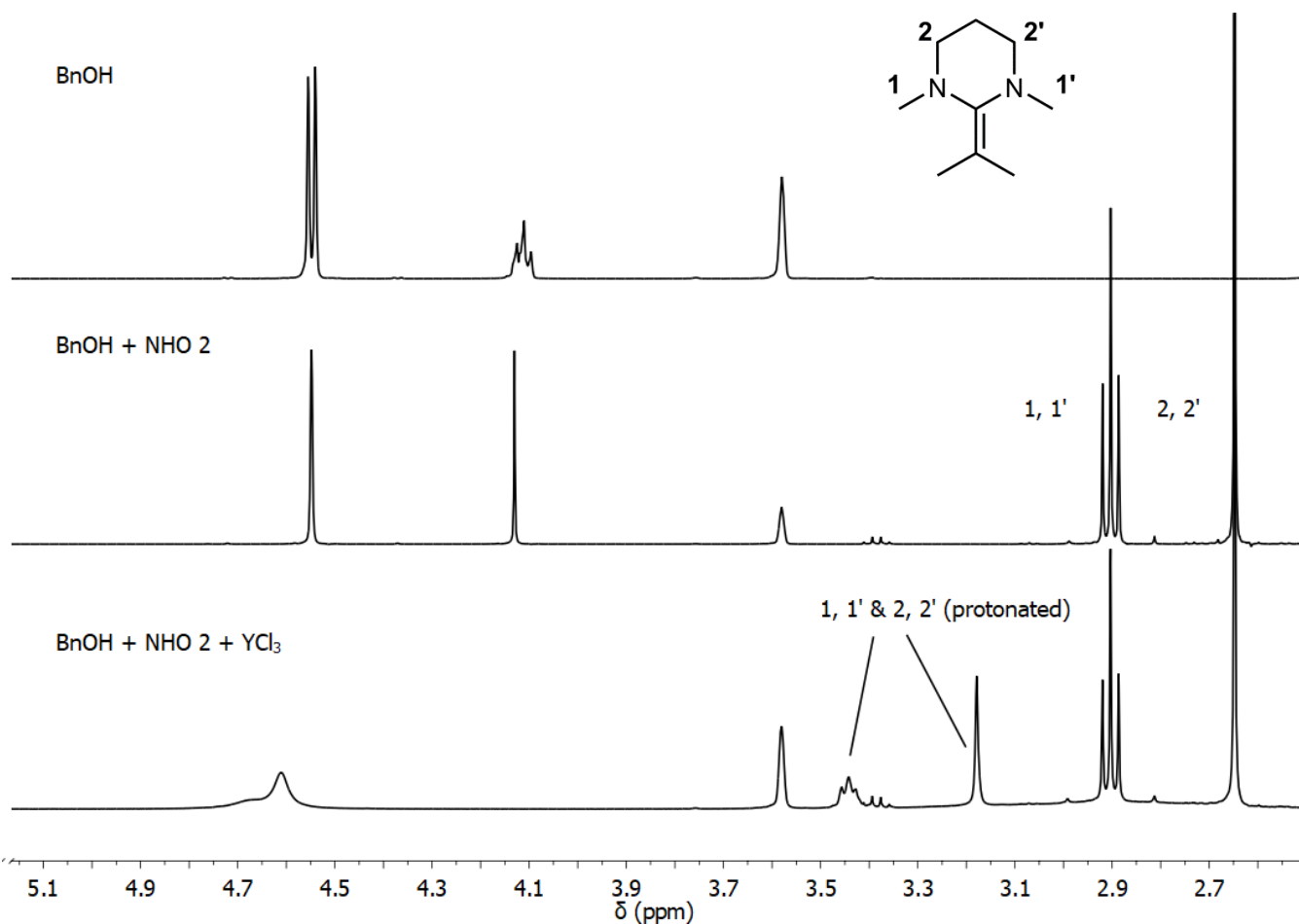


Figure S19. Complexation experiments with **2** and various Lewis Acids, as well as the ^1H -NMR spectrum of the initiator BnOH.

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