

Poly(ϵ -caprolactone-*co*- ω -pentadecalactone) electrospun fibers

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S1. General experimental remarks

All of the synthetic and polymerization experiments were conducted under an argon atmosphere. Toluene was refluxed with Na/benzophenone/dibenzo-18-crown-6 and distilled prior to use. 1,2-Dichloroethane was washed with Na₂CO₃ (aq.), stored over CaCl₂ and distilled with P₂O₅. Formic acid ($\geq 99.8\%$), acetic acid ($\geq 99.8\%$) and ethanol (99.5%) were used as purchased (Merck, NJ, USA). Hexafluoroisopropanol (99.5%, P&M Invest, Moscow, Russian Federation) was distilled prior to use. BHT-Mg catalyst [(BHT)Mg(μ -OBn)(THF)]₂ was prepared according previously described method.¹

CDCl₃ (Cambridge Isotope Laboratories, Inc., D 99.8 atom %) was used as purchased. The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks.

GPC measurements of the polymers were performed in 1,2,4-trichlorobenzene with a flow rate of 1 ml min⁻¹ at 50 °C using an Agilent PL-GPC 220 integrated instrument with an autosampler and RI detector. Calibration was achieved using polystyrene standards.

S2. Polymerization and polymer characteristics

Calculated amount of ω PDL or ω PDL/ ϵ CL mixture was placed into two-necked flask filled with argon, and heated to 100 °C. Calculated amount of the catalyst [(BHT)Mg(μ -OBn)(THF)]₂ in toluene (0.05 M solution) was added by syringe. After 2 h of the reaction at 100 °C the mixture was cooled. The product was dissolved in toluene at 110 °C (ω -PDL homopolymer) or in CHCl₃ at 60 °C (ω -PDL/ ϵ -CL copolymer). Three volumes of methanol containing 5 eq. of AcOH were added with stirring. The sediment was separated and re-

¹ I. E. Nifant'ev, A. V. Shlyakhtin, V. V. Bagrov, M. E. Minyaev, A. V. Churakov, S. G. Karchevsky, K. P. Birin and P. V. Ivchenko, *Dalton Trans.*, 2017, **46**, 12132.

precipitated by the same manner. The polymer obtained was dried *in vacuo* (12 h, 1 Torr) to remove methanol.

The examples of ^1H NMR spectra of homo- and copolymers obtained are presented in Figures S1–S3.

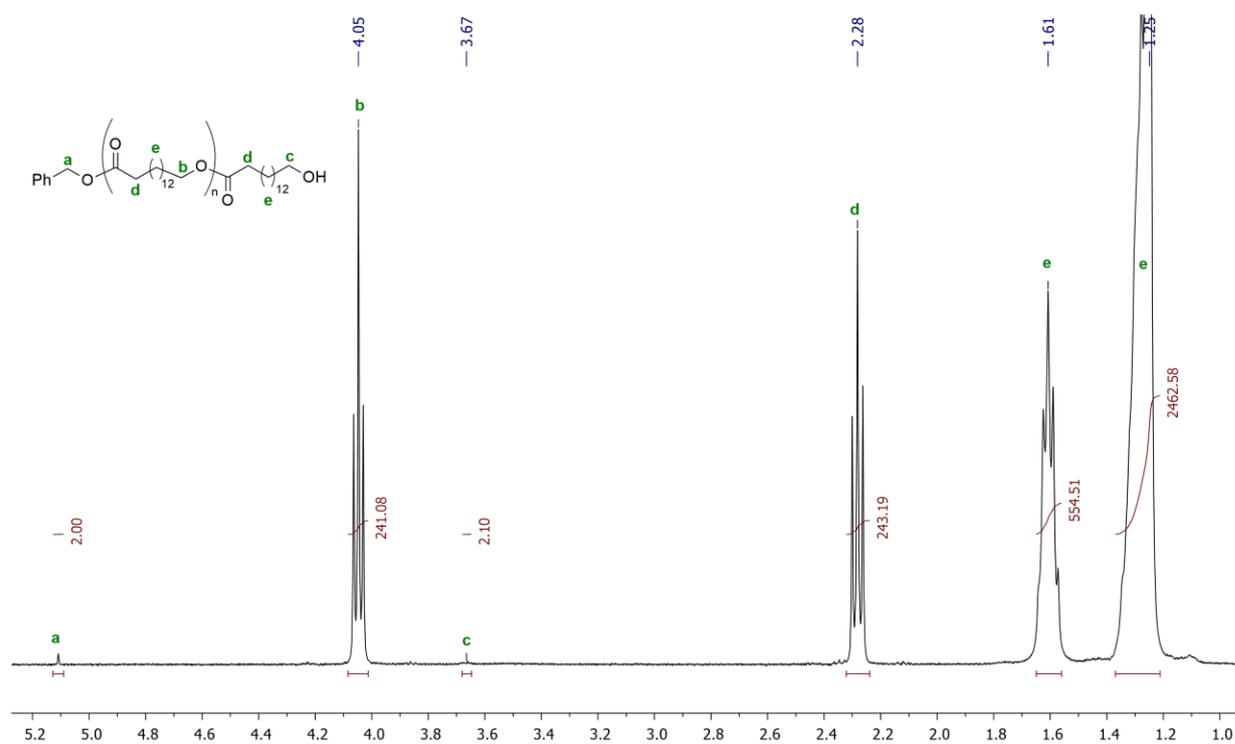


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3 , 20 $^\circ\text{C}$) of poly(ω PDL) ($P_n \sim 100$, Table 1, run 1)

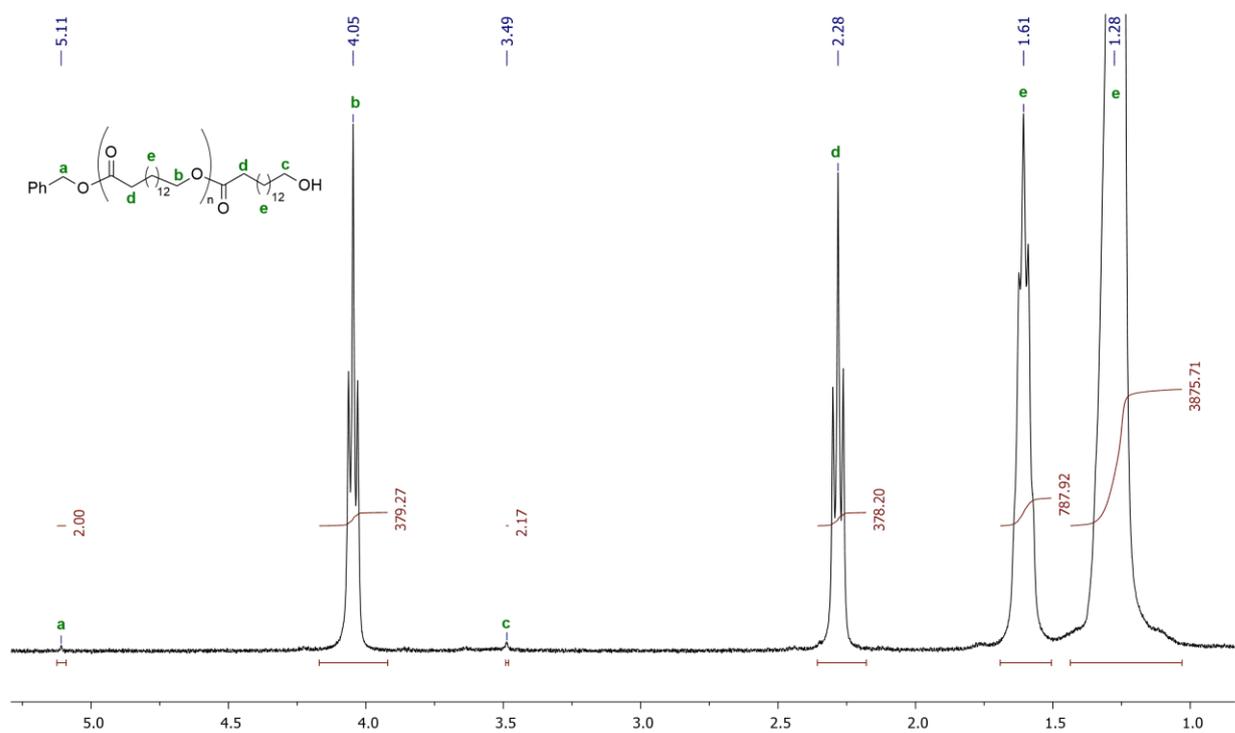


Figure S2. ^1H NMR spectrum (400 MHz, CDCl_3 , 20 $^\circ\text{C}$) of poly(ω PDL) ($P_n \sim 200$, Table 1, run 3)

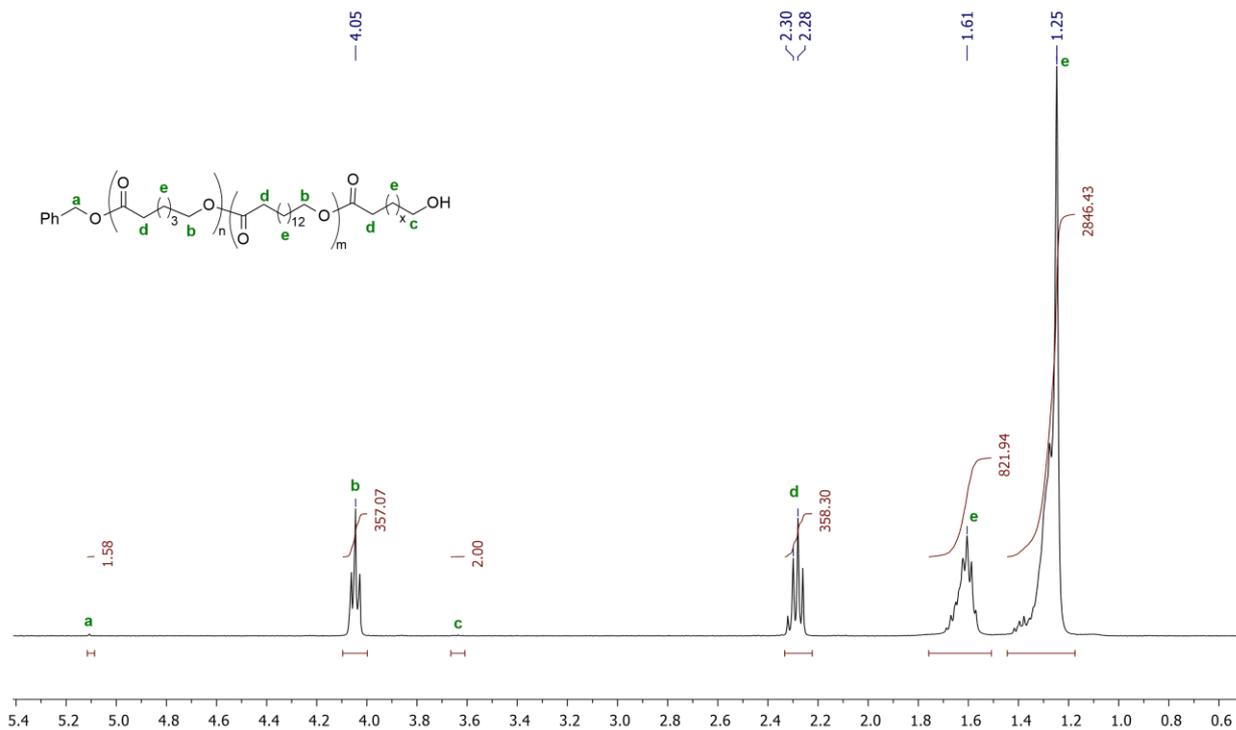


Figure S3. ¹H NMR spectrum (CDCl₃) of poly(ωPDL-co-εCL) (P_n~150/50, Table 1, run 5)

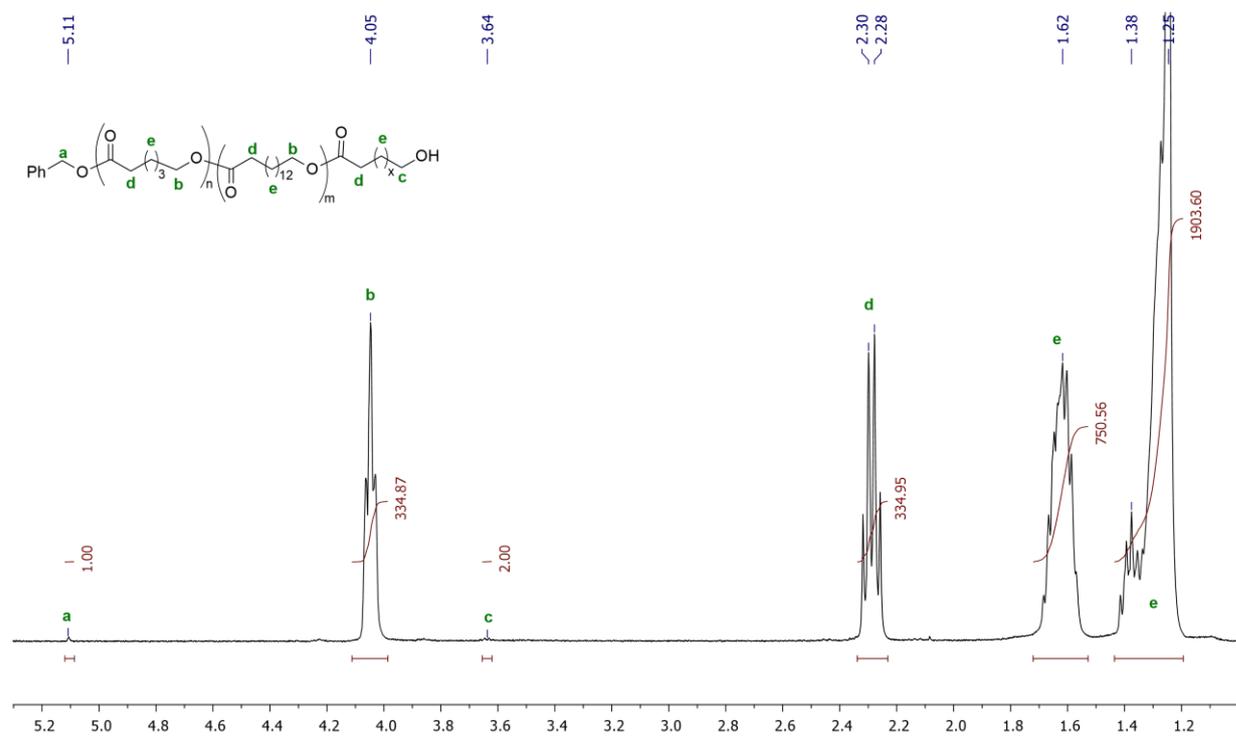


Figure S4. ¹H NMR spectrum (CDCl₃) of poly(ωPDL-co-εCL) (P_n~100/100, Table 1, run 6)

S3. Electrospinning

Electrospinning was performed using original laboratory device equipped with high-voltage power supply adapters (–20 kV and 50 kV), stepping motor (70 cm amplitude of the plate) and syringe dosage system (linear translators with plungers equipped with stepping motor). Stainless steel needles ($d = 0.8$ mm) were used in ES experiments.

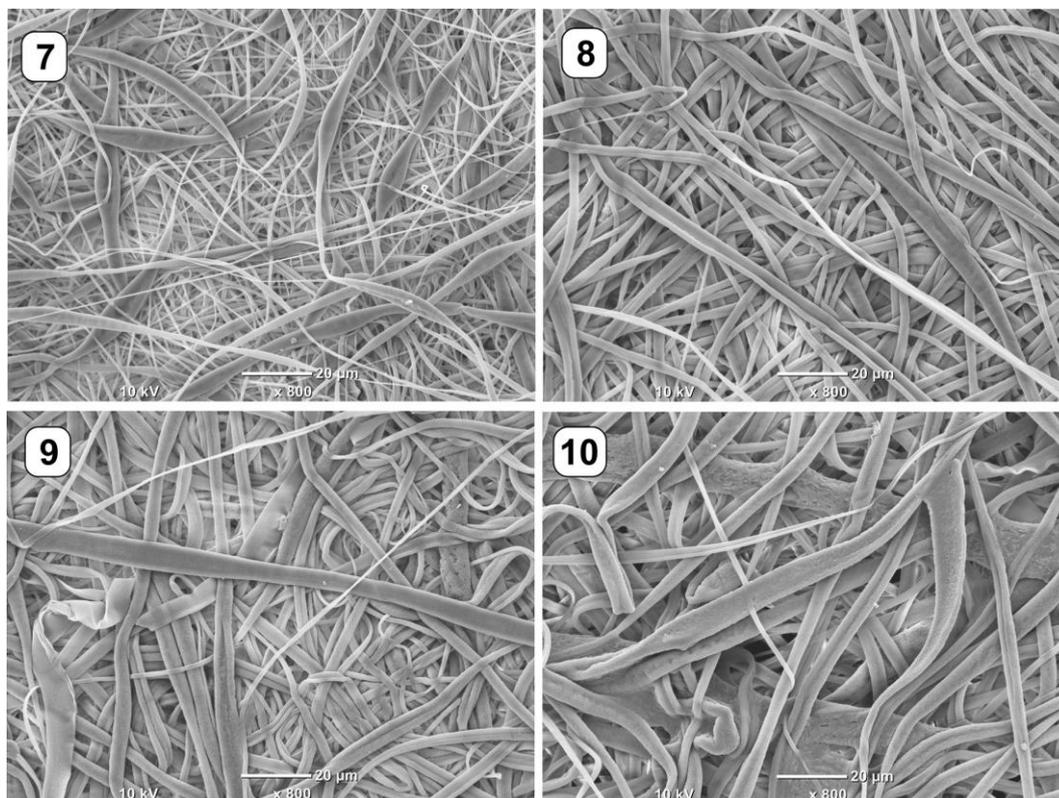


Figure S5. ES fibers obtained from poly(ω PDL) samples (Table 2, runs 7–10)

Table S1 Electrospinning of polymer solutions ^{a)}

Run	ω PDL/ ε CL ^{b)}	S1 ^{c)}	S2 ^{c)}	S1/S2
1	150/50	CHCl ₃	EtOH	9:1
2	150/50	C ₂ H ₄ Cl ₂	EtOH	9:1
3	150/50	C ₂ H ₄ Cl ₂	EtOH	9:1 ^{d)}
4	150/50	HFIP	–	–
5	150/50	C ₂ H ₄ Cl ₂	HFIP	4:1
6	100/100	C ₂ H ₄ Cl ₂	HFIP	4:1
7	100/0	C ₂ H ₄ Cl ₂	HFIP	4:1
8	150/0	C ₂ H ₄ Cl ₂	HFIP	4:1
9	200/0	C ₂ H ₄ Cl ₂	HFIP	4:1
10	300/0	C ₂ H ₄ Cl ₂	HFIP	4:1

^{a)} Parameters of ES experiments: needle/plate potentials –4–16 kV, plate amplitude 4 cm, plate speed 5 cm s⁻¹, the distance between plate and needle 10 cm, the feed rate 6 ml h⁻¹. ^{b)} Comonomer molar ratio relative to mol of Mg. ^{c)} S1, S2 – solvents used in preparation of 10% (wt.) polymer solutions. ^{d)} 1% HCOOH was added.