

## **Discovering New Block Terpolymer Micellar Morphologies**

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*Electronic supplementary information*

## Experimental details

### Materials

2-Ethylhexanoyl chloride and 2-chloroethylammonium chloride were purchased from Sigma-Aldrich and used as received. 2-Ethyl-2-oxazoline and methyl tosylate were obtained from Acros, distilled to dryness over barium oxide (BaO), and stored under argon.

### General methods and instrumentation

The Initiator Sixty single-mode microwave synthesizer from Biotage, equipped with a noninvasive IR sensor (accuracy:  $\pm 2\%$ ), was used for polymerizations under microwave irradiation. Microwave vials were heated to 110 °C overnight, cooled to room temperature and filled with argon before usage. All polymerizations were carried out with temperature control. Size exclusion chromatography (SEC) was performed on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump and a RID-10A refractive index detector using a solvent mixture containing chloroform, triethylamine and isopropanol (94:4:2) as eluent at a flow rate of 1 mL min<sup>-1</sup> on a PSS-SDV-linear M 5  $\mu$ m column at room temperature. Molar masses were calculated against polystyrene standards. For preparative SEC, Bio-Beads S-X1 (crosslinked polystyrene beads) from Bio-Rad were used. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the products were recorded on a Bruker AC 250 MHz or AC 400 MHz spectrometer at room temperature, with CDCl<sub>3</sub> as the solvent. The chemical shifts are given in ppm relative to the signal from residual non-deuterated solvent. For the MALDI measurements, an Ultraflex III TOF/TOF apparatus (Bruker Daltonics, Bremen, Germany) was used. The instrument was equipped with a Nd:YAG laser and a collision cell. All spectra were measured in the positive reflector or linear mode. The instrument was calibrated prior to each measurement with an external cPMMA standard from PSS Polymer Standards Services GmbH (Mainz, Germany). Dynamic light scattering (DLS) data were collected with a Malvern CGS-3 equipped with a He-Ne laser (633 nm) at angles varying from 50° to 140°.

Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (LaB6 filament). Images were recorded with a bottom mounted 1k  $\times$  1k Gatan CCD camera. For cryoTEM measurements, 200 mesh carbon coated copper grids were purchased from SPI. Prior to blotting, the grids were made hydrophilic by surface plasma treatment using a Cressington 208 carbon coater operating at 5 mA for 40 s. For sample preparation a droplet of the micelle solution was blotted onto the grid and subsequently excess liquid was manually removed with filter paper. The samples were not stained.

### Monomer synthesis

***N*-(2-Chloroethyl)-2-ethylhexanamide (1)**: Under argon, 13.49 g (83 mmol) 2-ethylhexanoyl chloride and 9.75 g (0.084 mol) 2-chloroethylammonium chloride were suspended in 200 mL dichloromethane and cooled to -5 °C. Subsequently, 26.6 mL (19.37 g, 191 mmol) triethylamine were added dropwise within one hour, the reaction mixture was stirred for three hours, and the reaction was terminated by adding 70 mL water. The aqueous phase was extracted twice with 50 mL dichloromethane, and the combined organic phases were washed with water and brine. After drying over MgSO<sub>4</sub>, the solvent was removed under reduced pressure, and the crude product was used without further purification.

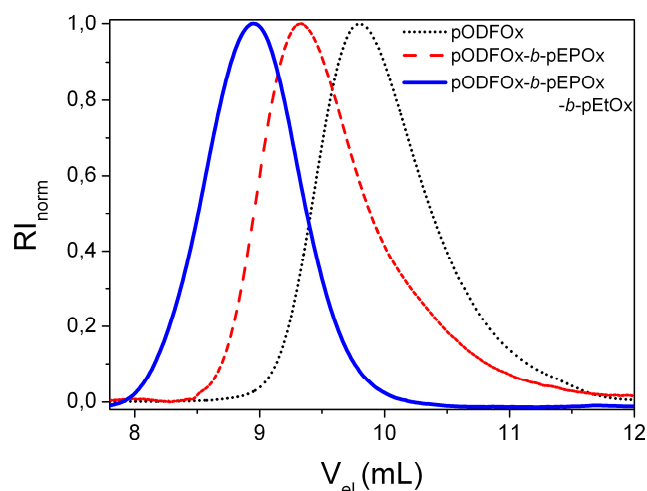
**2-(1-Ethylpentyl)-2-oxazoline (EPOx)**: To a 25 wt.-% solution of KOH in water, a solution of 20.4 g of the crude product **1** (100 mmol) in 200 mL THF was added dropwise, and the sample was heated to 50 °C for 16 h. After cooling to ambient temperature, the aqueous phase was extracted twice with diethyl ether. Subsequently, the combined organic phases were

washed three times with water and once with brine. After drying the sample over  $\text{MgSO}_4$ , the solvent was removed under reduced pressure, and the crude product was purified by distillation ( $67\text{ }^\circ\text{C}$ ,  $5.5 \times 10^{-2}$  Torr) to give 10.9 g (0.065 mol) of EPOx in 78% yield (related to the 2-ethylhexanoyl chloride).

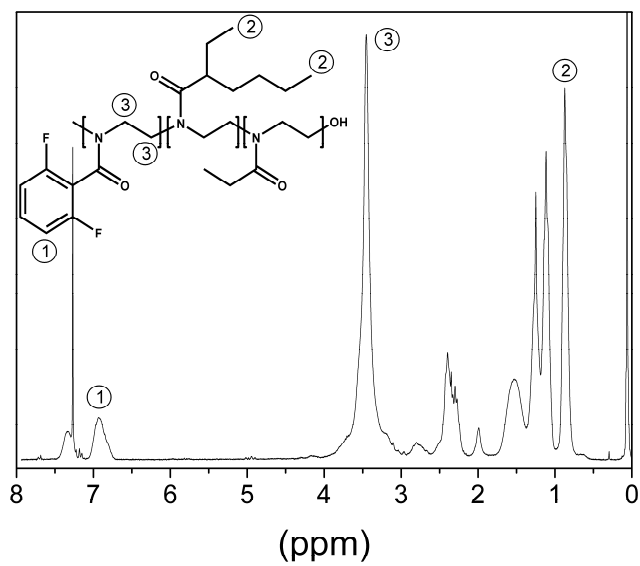
$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta = 4.2$  (t,  $^3J(\text{H}, \text{H}) = 9.6$  Hz, 2H,  $\text{CH}_2$ ), 3.8 (t,  $^3J(\text{H}, \text{H}) = 9.6$  Hz, 2H,  $\text{CH}_2$ ), 2.3 (quintet,  $^3J(\text{H}, \text{H}) = 7.6$  Hz, 1H, CH), 1.6 (m, 4H,  $\text{CH}_2$ ), 1.3 (m, 4H,  $\text{CH}_2$ ), 0.88 (m, 6H,  $\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta = 170.1, 68.1, 54.6, 37.4, 29.2, 24.8, 22.8, 19.6, 14.5, 12.7$ . Elemental analysis: calcd. C 70.96, H 11.31, N 8.28; found C 70.92, H 11.42, N 8.25.

### Microwave-assisted copolymerization

For the synthesis of the triblock copoly(2-oxazoline)  $\text{p}(\text{ODFOx})_{20}\text{-}b\text{-p}(\text{EPOx})_{20}\text{-}b\text{-p}(\text{EtOx})_{40}$  a stock solution of 16 mg methyl tosylate (0.086 mmol), 332 mg ODFOx (1.8 mmol) and 5 g nitromethane (81.97 mmol) was prepared and divided over six polymerization vials. All six vials were exposed to microwave radiation for a pre-calculated time to obtain near-quantitative conversion ( $\ln [M]_0/[M]_t = 4$ ). For control purposes, in two vials the polymerization was quenched by addition of 50  $\mu\text{L}$  water. Subsequently, 55.44 mg EPOx (0.32 mmol) were added via a syringe to the other vials. Analogous to the first step, all four samples were subjected to microwave irradiation, the second polymerization was terminated in two of the vials, and 64.9 mg EtOx (0.66 mmol) were transferred to the remaining two vials which again were subjected to microwave irradiation, in order to obtain the desired triblock copolymer  $\text{p}(\text{ODFOx})_{20}\text{-}b\text{-p}(\text{EPOx})_{20}\text{-}b\text{-p}(\text{EtOx})_{40}$ .  $^1\text{H-NMR}$  spectroscopy was used to confirm the absence of residual monomer as well as to investigate the polymer composition. The full conversion of each class of monomers as well as the molar mass distribution after each polymerization step was investigated using GC and SEC, respectively. The triblock copolymers obtained were purified by preparative size exclusion chromatography.



**Fig. S1** SEC traces for the synthesis of the triblock copolymer  $\text{pODFOx}_{23}\text{-}b\text{-pEPOx}_{28}\text{-}b\text{-pEtOx}_{49}$  (RI detector;  $\text{CHCl}_3\text{:isopropanol:NEt}_3 = 94\text{:}2\text{:}4$  as eluent).



**Fig. S2** <sup>1</sup>H NMR spectrum of the triblock copolymer (in CDCl<sub>3</sub>). The mol percentages of each block were determined by means of the integrals of the assigned peaks to be pODFO<sub>x23</sub>-*b*-pEPO<sub>x28</sub>-*b*-pEtO<sub>x49</sub>.