Supporting Information for
Microstructure Analysis of Biocompatible Phosphoester-co-polymers

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\textbf{Fig. S1.} Experimental setup for the oxidation of 2-chloro-1,3,2-dioxaphospholane.
Fig. S2. $^{31}$P NMR spectrum of a) EEP and b) EMEP in DMSO-$d_6$. 
Fig. S3. $^1$H NMR spectrum of EMEP in CDCl$_3$. 
Fig. S4. $^1$H NMR spectrum of P(EEP$_{17}$-co-EMEP$_{16}$) in DMSO-$d_6$. 
**Fig. S5.** SEC chromatograms of a) P(EEP-co-EMEP) copolymers and b) PEMEP homopolymers (measured in DMF at 50 °C and a flow rate of 1.0 mL min⁻¹). Periodic artifacts are due to highly diluted samples (1.0 mg mL⁻¹, 100 µL injected) and the high measuring sensitivity of the employed RI detector.
**Fig. S6.** Graphical representation of the measured $T_g$ of all copolymers.
Fig. S7. Dyad analysis with all possible head-to-head (above) and tail-to-tail (bottom) configurations of PEMEP.
**Fig. S8.** $^{31}$P NMR of all copolymers. a) Magnification of the tail-to-tail region. b) Zoom in the region assigned to the EMEP$_{a}$-EMEP$_{b}$ dyad.
**Fig. S9.** Tail-to-tail microstructures resulting in different chemical shifts in $^{31}$P NMR (compare to Fig. S8, ESI)
Fig. S10. $^1$H$^{31}$P HMBC spectra of five representative examples in DMSO-$d_6$: a) PEEP$_{32}$, b) P(EEP$_{28}$-co-EMEP$_5$); c) P(EEP$_{17}$-co-EMEP$_{16}$); d) P(EEP$_{4}$-co-EMEP$_{29}$); e) PEMEP$_{38}$. 

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**Fig. S11.** $^1$H DOSY of five representative examples in DMSO-$d_6$: a) PEEP$_{32}$, b) P(EEP$_{28}$-co-EMEP$_{5}$); c) P(EEP$_{17}$-co-EMEP$_{16}$); d) P(EEP$_{4}$-co-EMEP$_{20}$); e) PEMEP$_{38}$. The diffusion coefficient calculated by Bayesian DOSY Transformation is for all copolymers in the same range.
Fig. S12. Change in transmittance of PEMEP solutions with different molecular weights. Cloud points were determined in PBS pH 7.4 (10 mM) prepared from MilliQ water (18.2 mΩ) at a concentration of 10.0 mg∙mL⁻¹. The heating/cooling rate was 1 °C·min⁻¹ and values were recorded every 0.1 °C.
Fig. S13. Change in transmittance of P(EEP-co-EMEP) copolymers at a concentration of 10 mg·mL⁻¹ in PBS pH 7.4 10 mM at 500 nm and a heating rate of 1°C·min⁻¹.