Electronic Supplementary Material (ESI) for Polymer Chemistry
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Supporting Information for

Microstructure Analysis of Biocompatible Phosphoester-*co*-polymers

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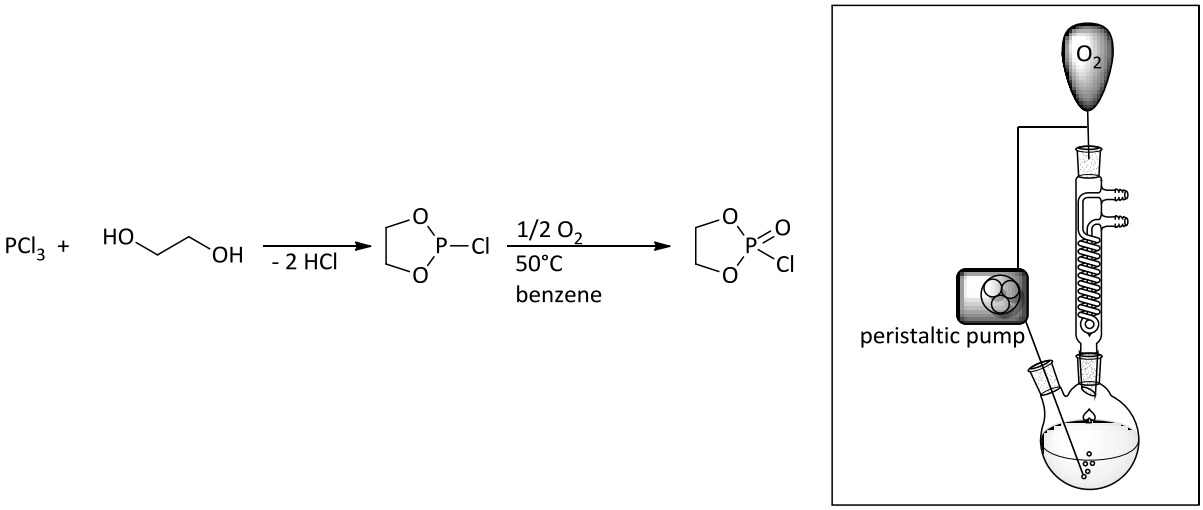

Fig. S1. Experimental setup for the oxidation of 2-chloro-1,3,2-dioxaphospholane.

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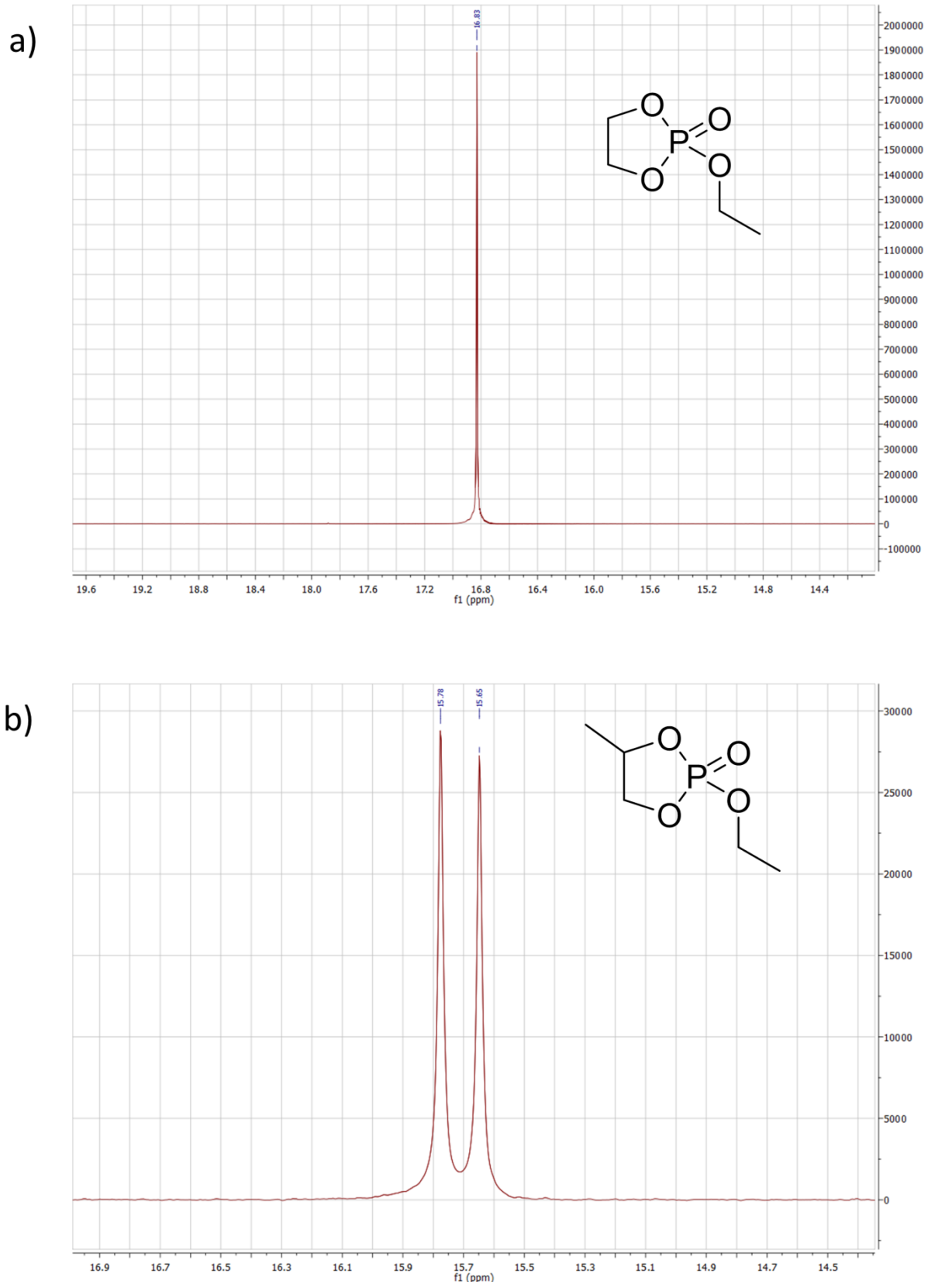

Fig. S2. ^{31}P NMR spectrum of a) EEP and b) EMEP in DMSO-d_6.

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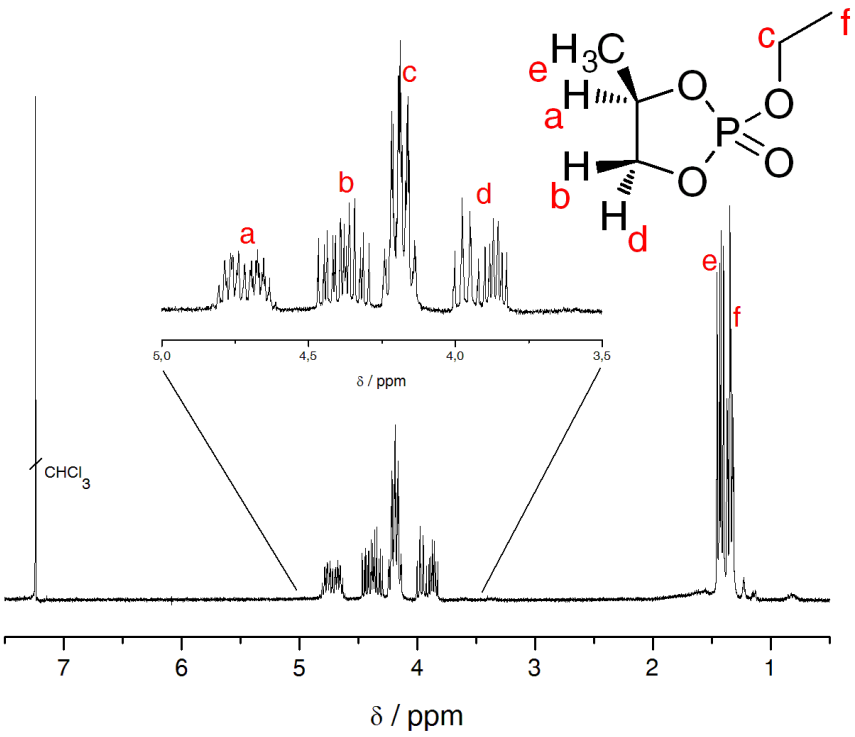

Fig. S3. ^{1}H NMR spectrum of EMEP in $CDCl_3$.

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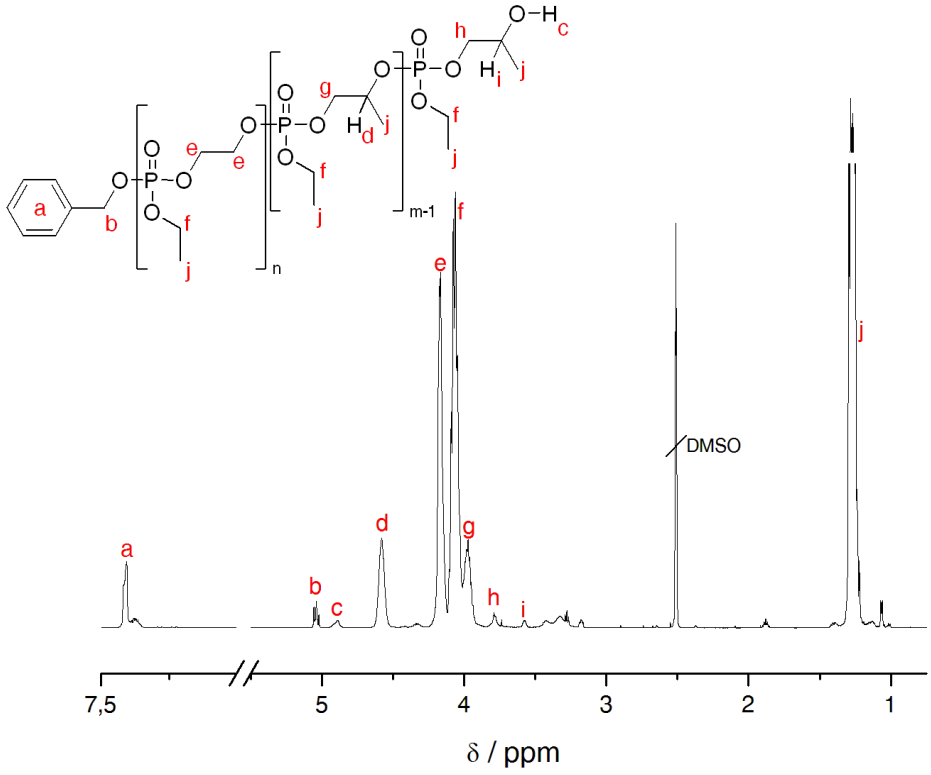

Fig. S4. ^{1}H NMR spectrum of P(EEP$_{17}$-*co*-EMEP$_{16}$) in DMSO-d_6.

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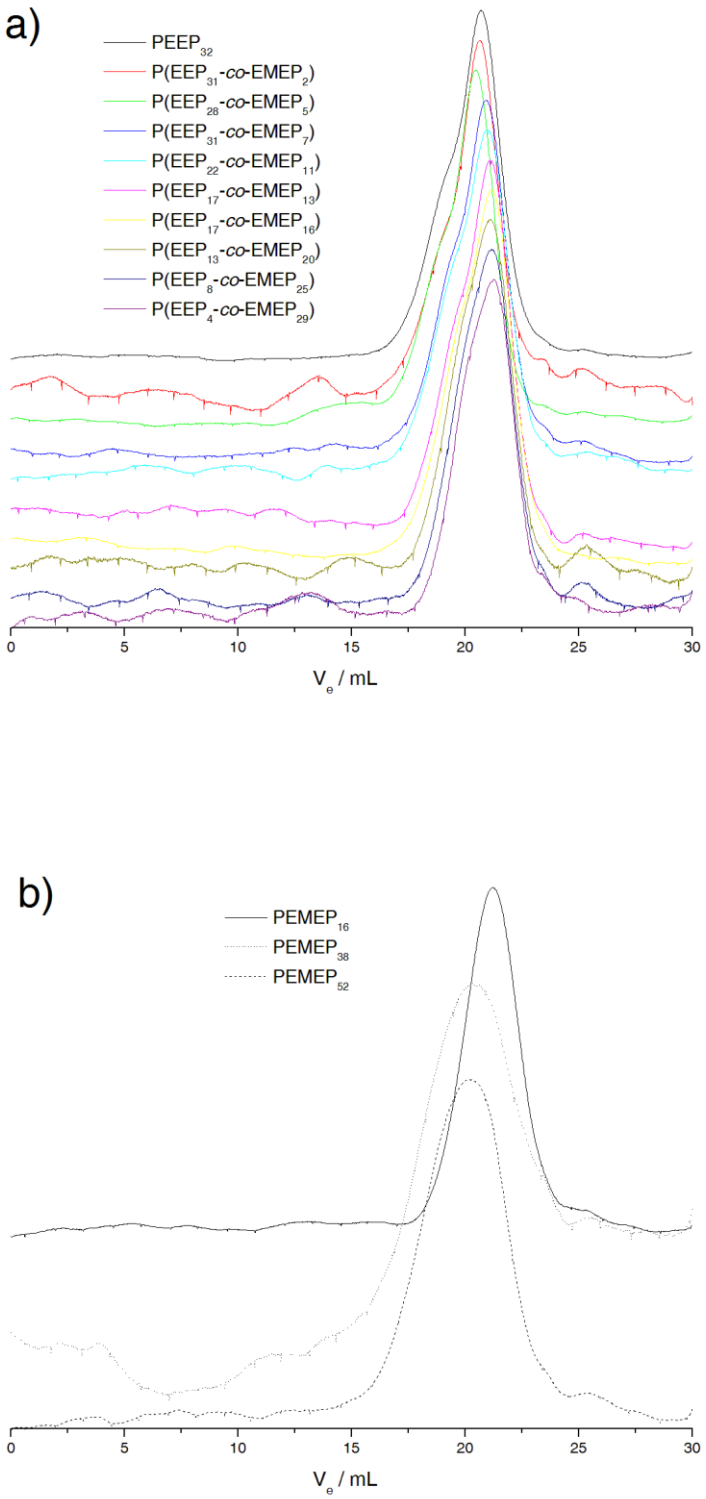

Fig. S5. SEC chromatograms of a) P(EEP-*co*-EMEP) copolymers and b) PEMEP homopolymers (measured in DMF at 50 °C and a flow rate of 1.0 mL·min^{-1}). Periodic artifacts are due to highly diluted samples (1.0 mg·mL^{-1}, 100 µL injected) and the high measuring sensitivity of the employed RI detector.

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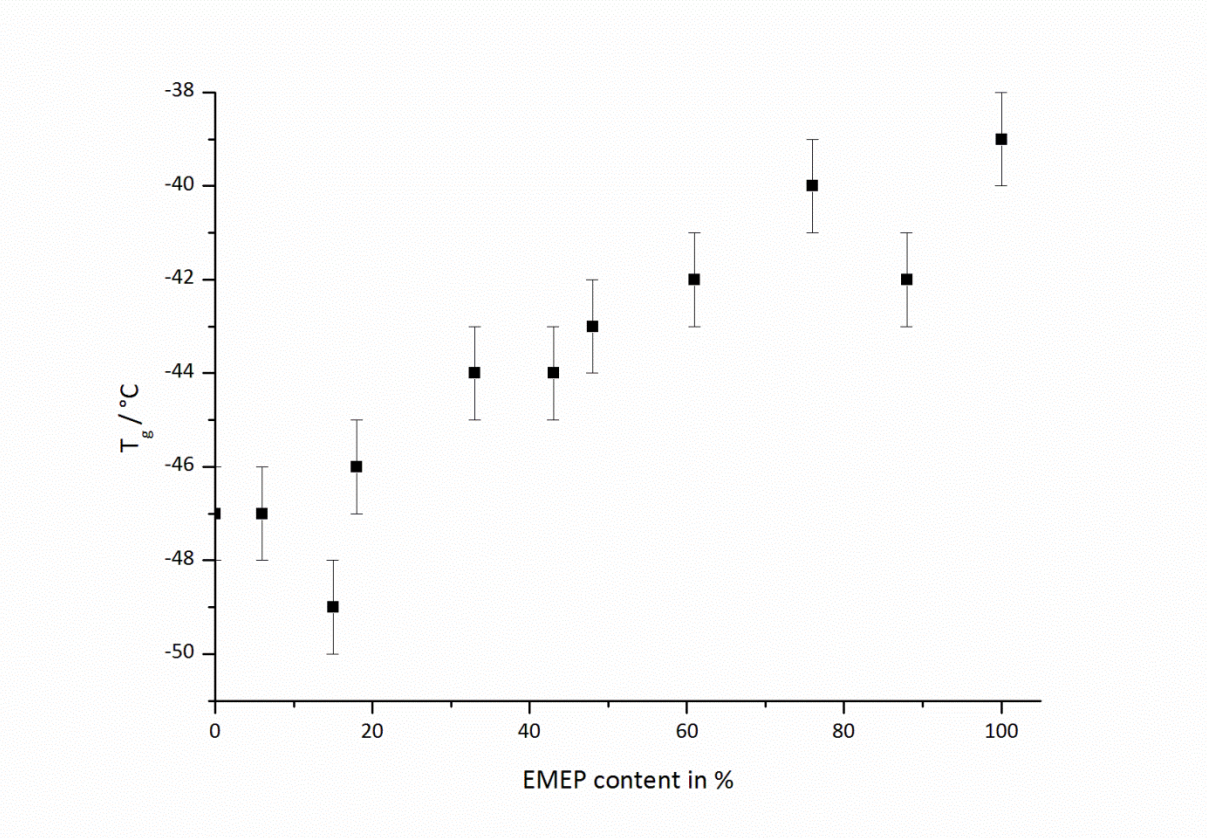

Fig. S6. Graphical representation of the measured T_g of all copolymers.

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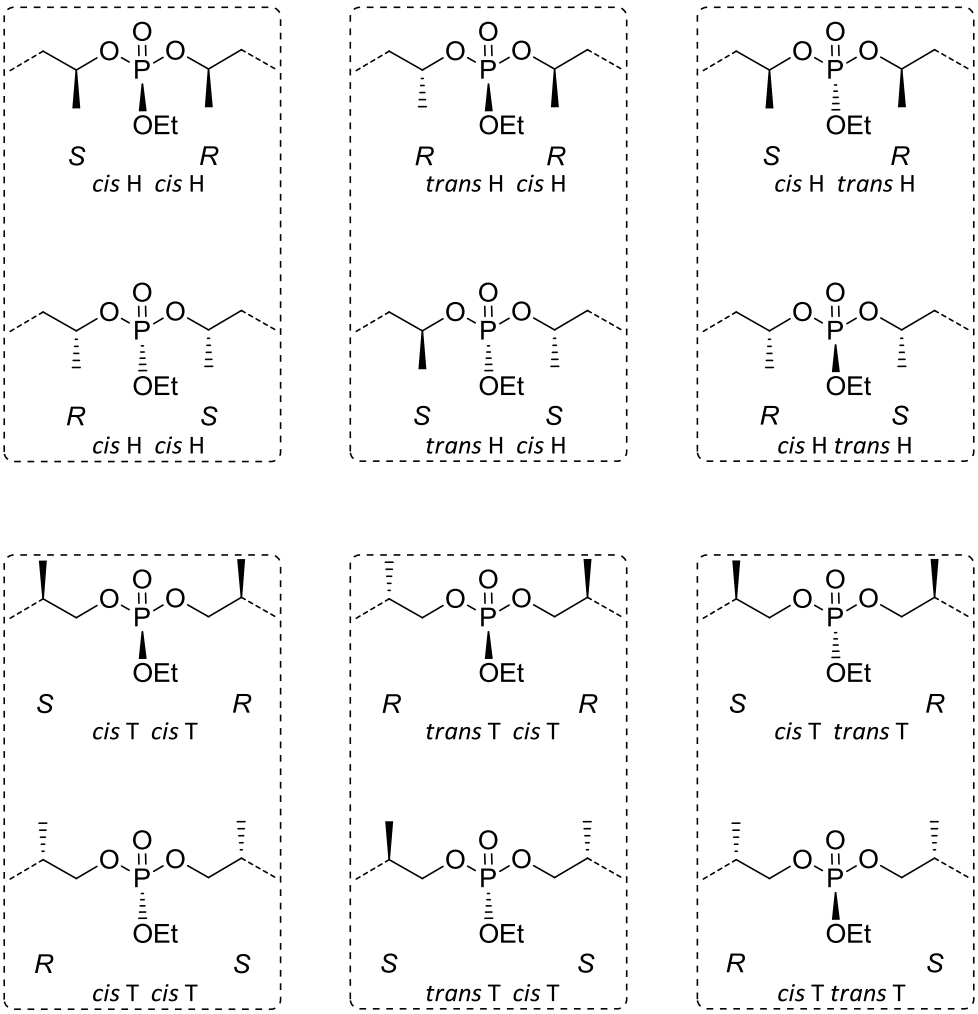

Fig. S7. Dyad analysis with all possible head-to-head (above) and tail-to-tail (bottom) configurations of PEMEP.

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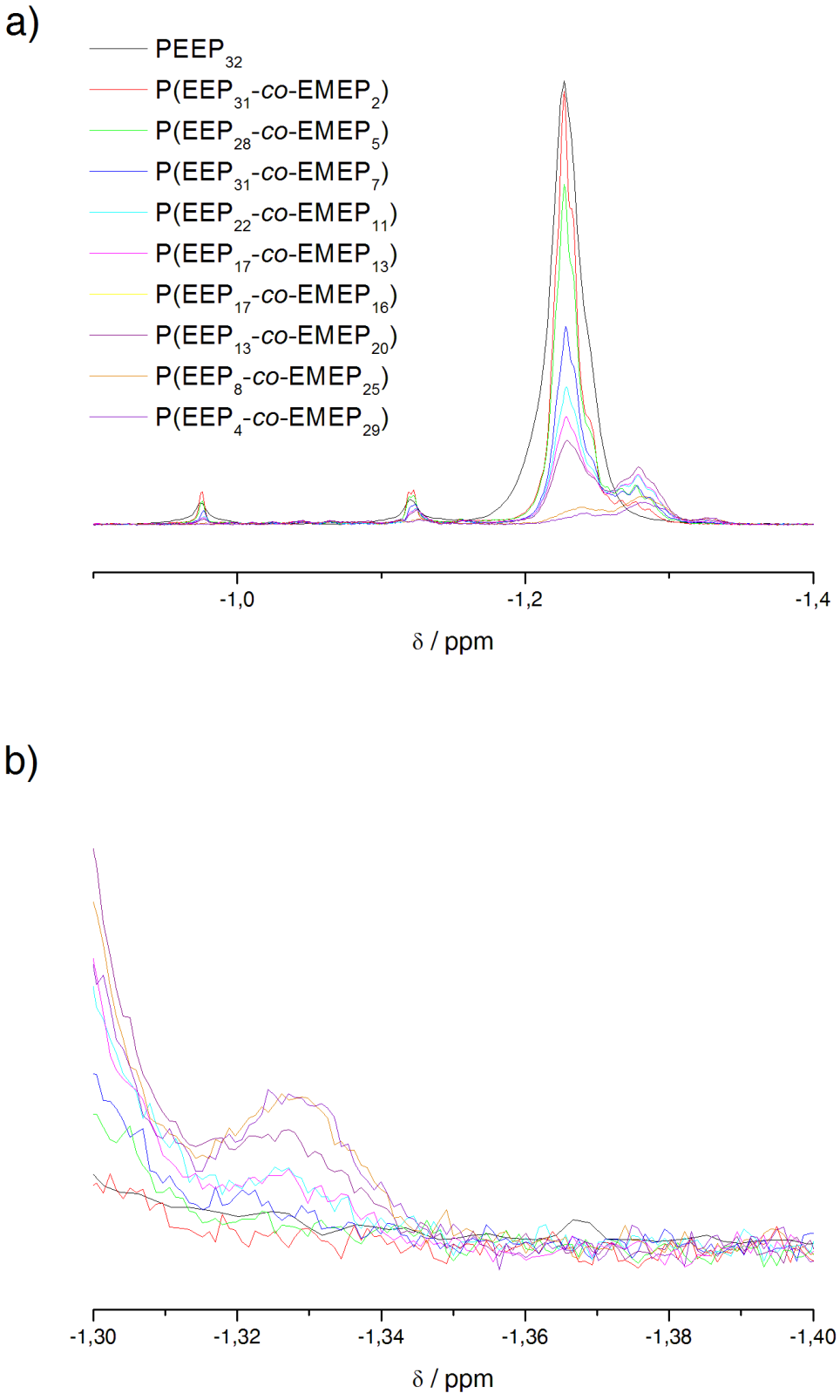

Fig. S8. ^{31}P NMR of all copolymers. a) Magnification of the tail-to-tail region. b) Zoom in the region assigned to the $EMEP_{\alpha}$-$EMEP_{\beta}$ dyad.

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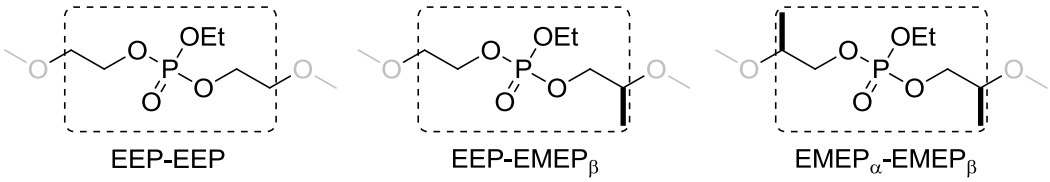

Fig. S9. Tail-to-tail microstructures resulting in different chemical shifts in ^{31}P NMR (compare to Fig. S8, ESI)

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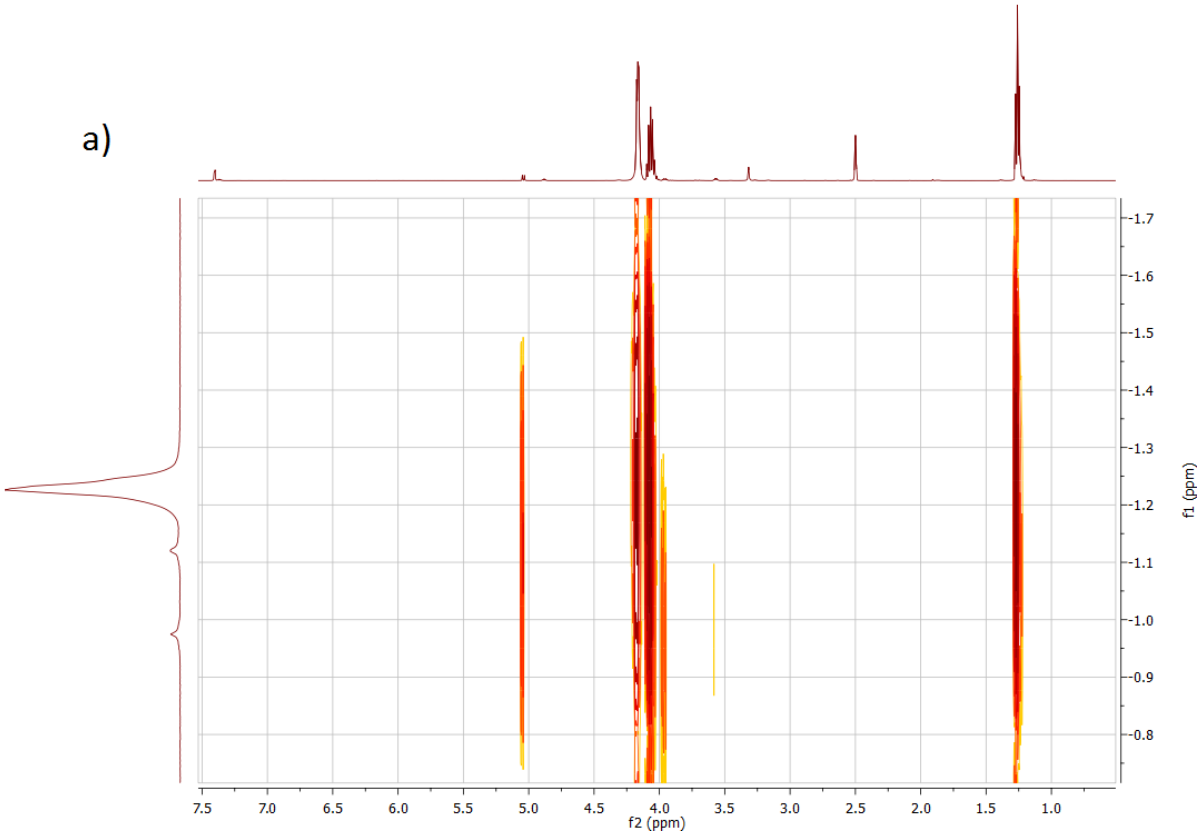
a)



b)

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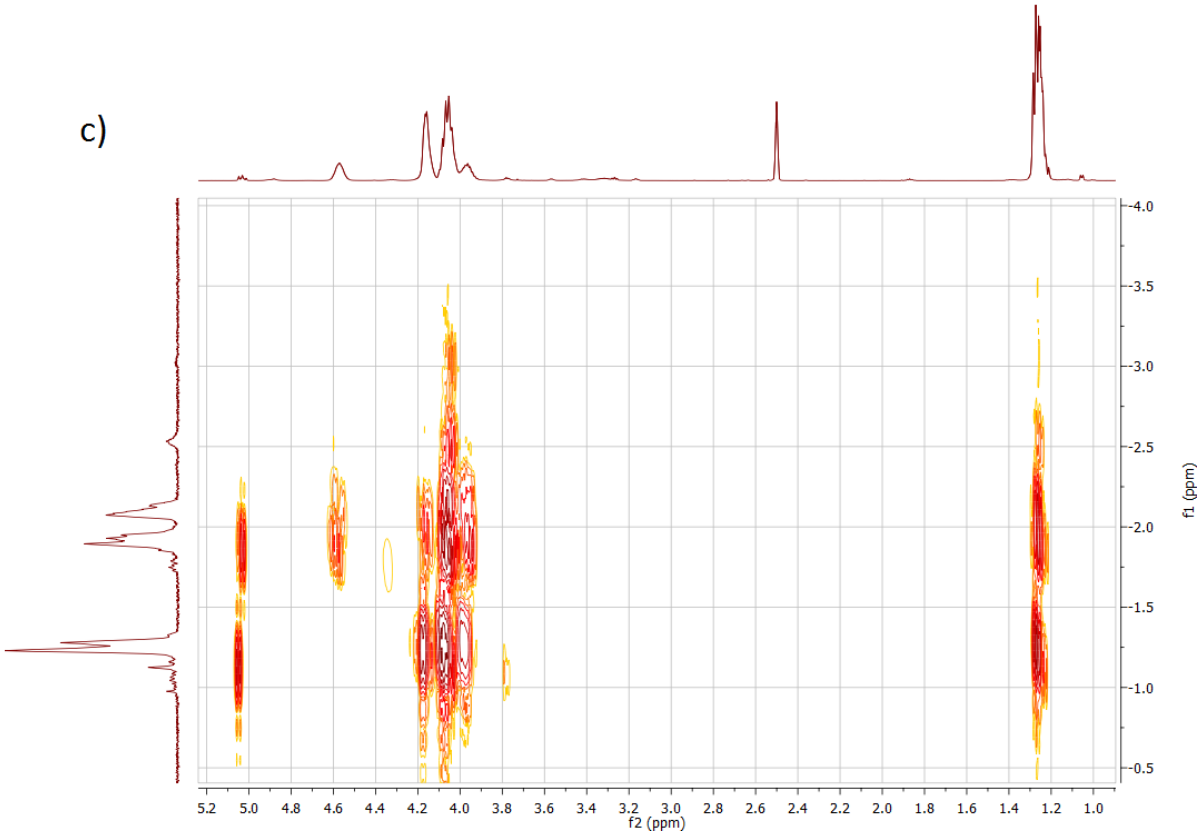

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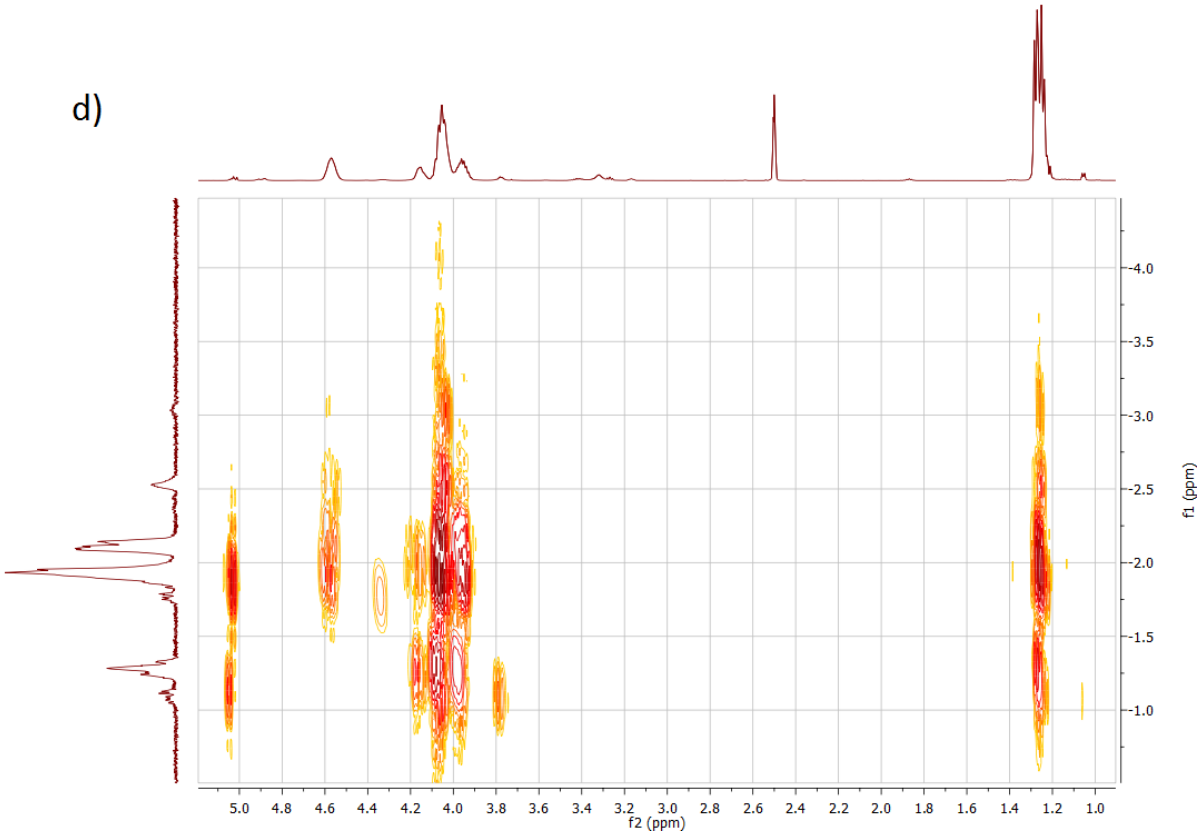

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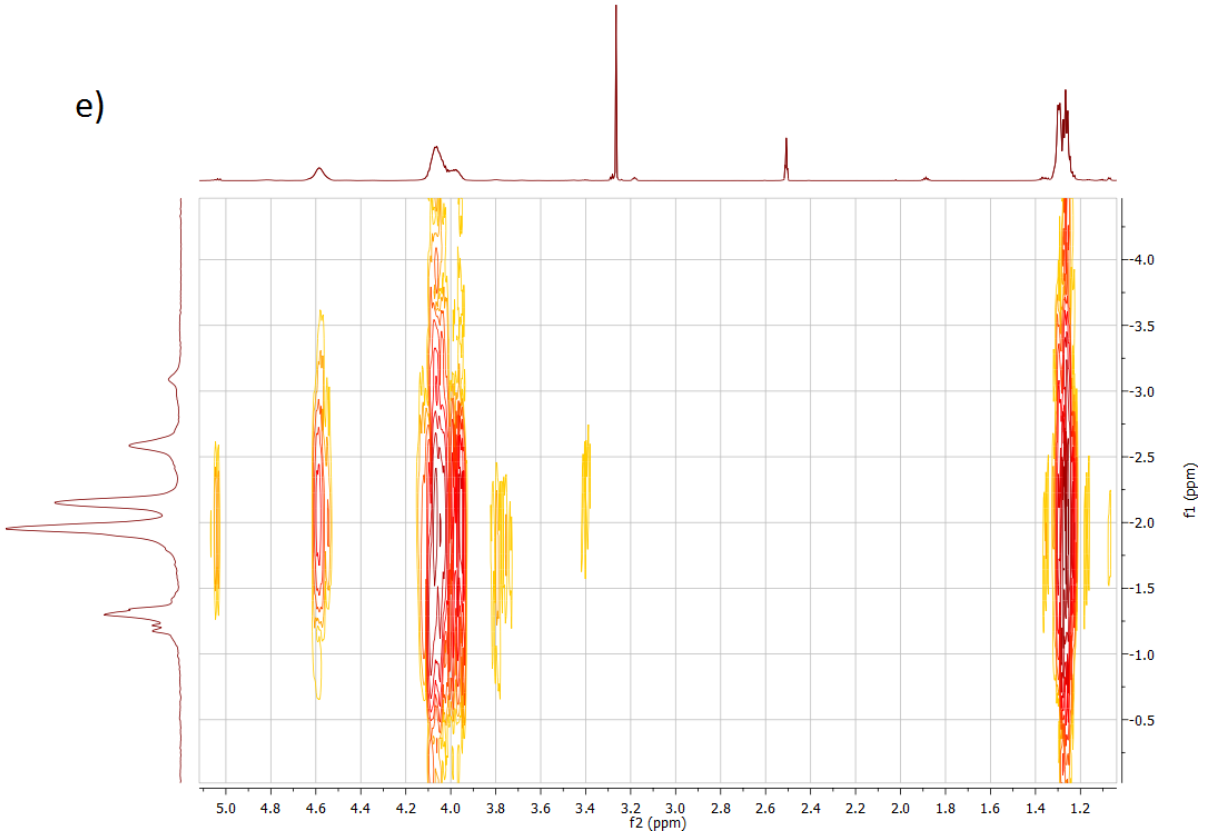

Fig. S10. $^{1}H^{31}P$ HMBC spectra of five representative examples in DMSO-d_6: a) $PEEP_{32}$, b) $P(EEP_{28}$-*co*-$EMEP_5)$; c) $P(EEP_{17}$-*co*-$EMEP_{16})$; d) $P(EEP_4$-*co*-$EMEP_{29})$; e) $PEMEP_{38}$.

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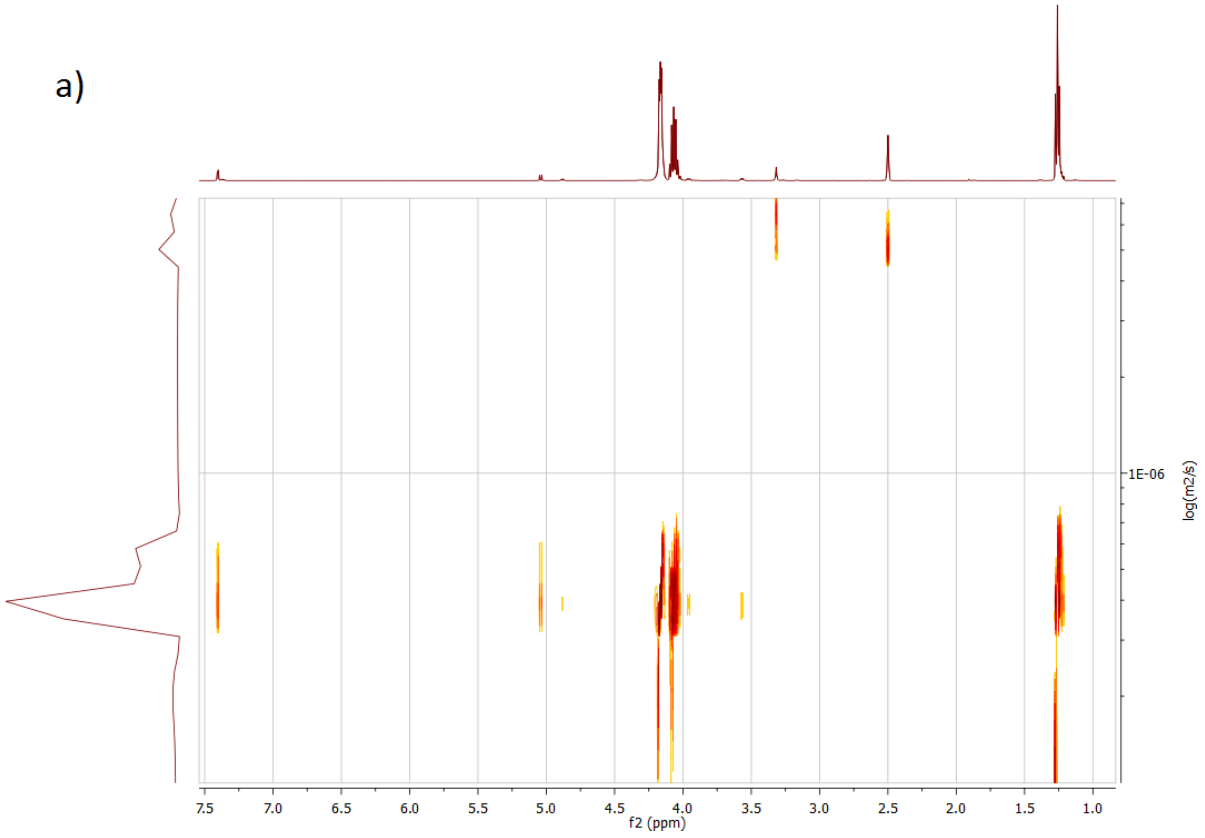

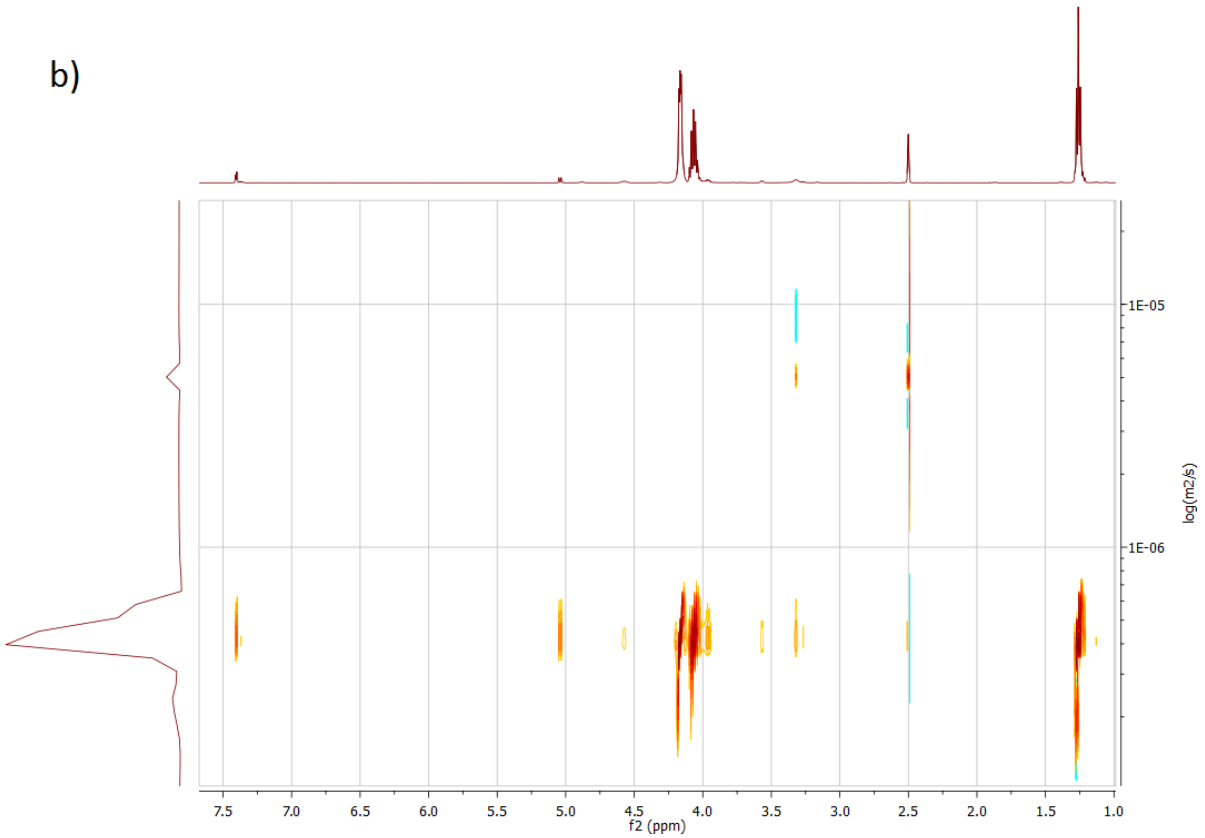

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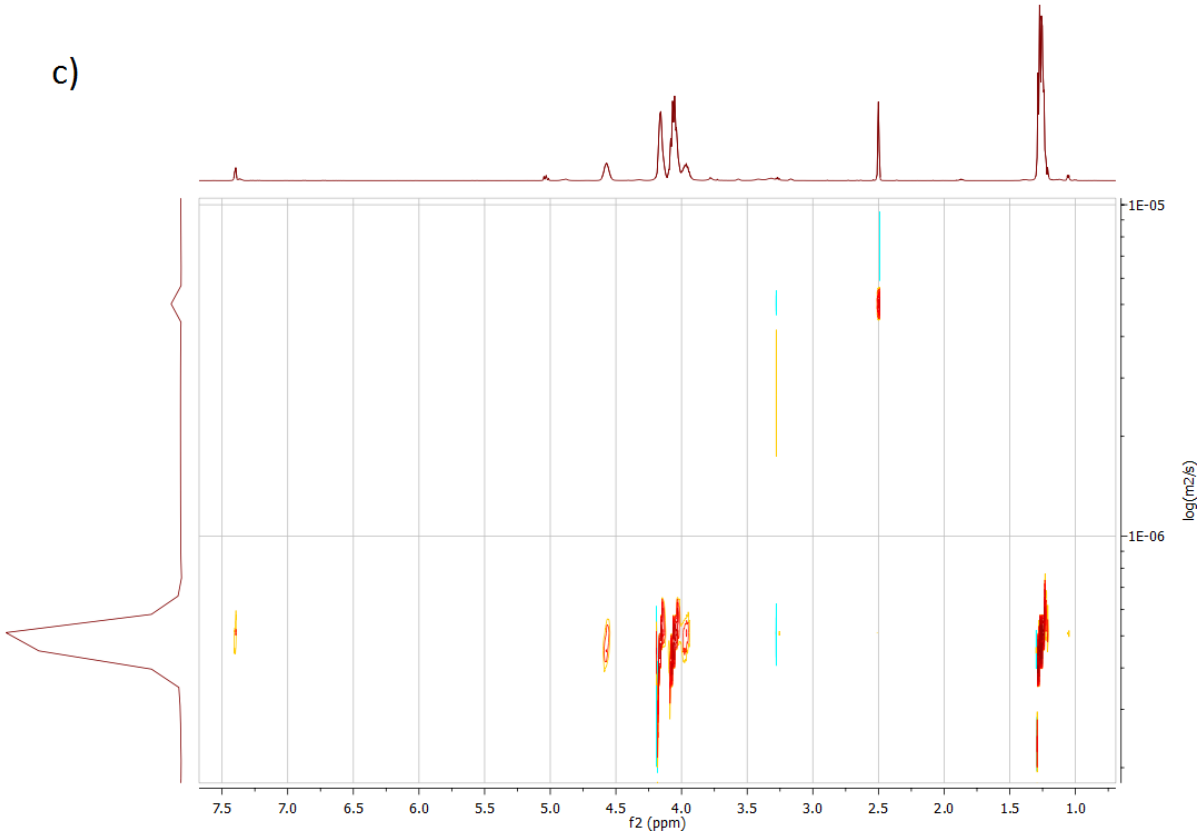

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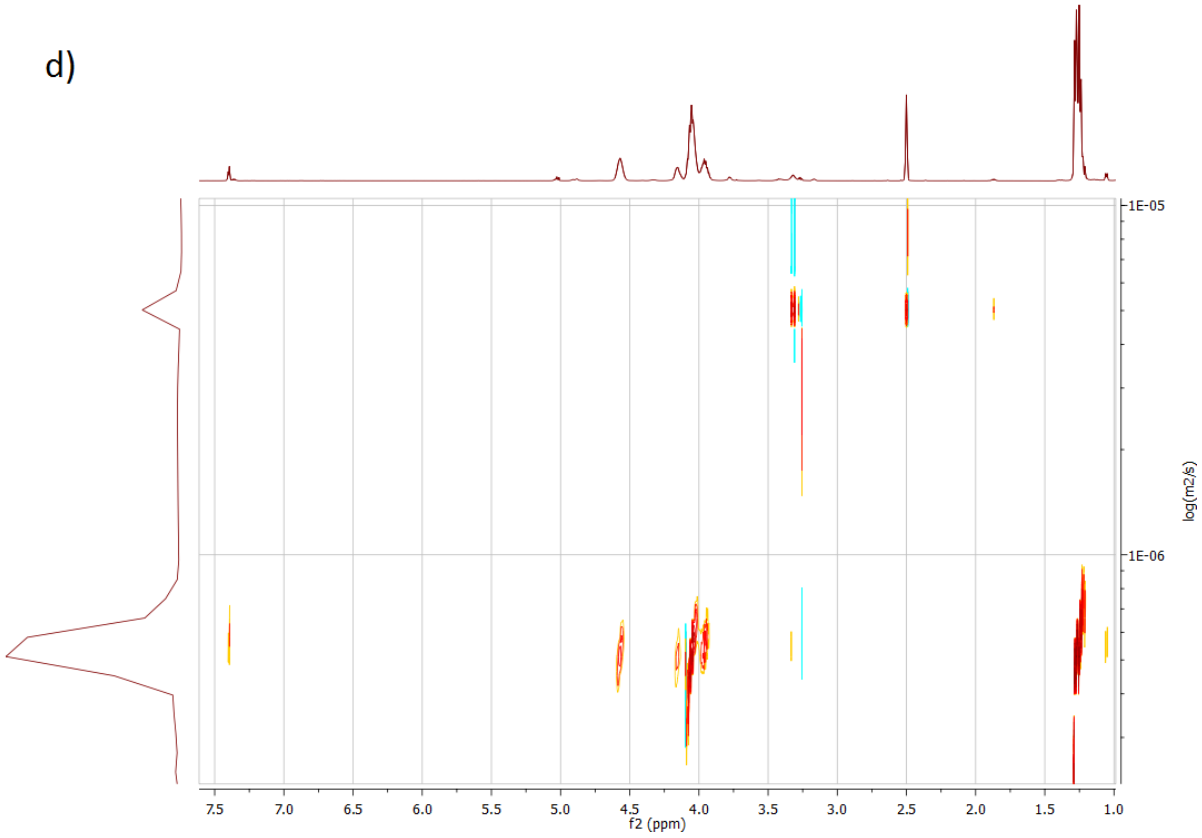

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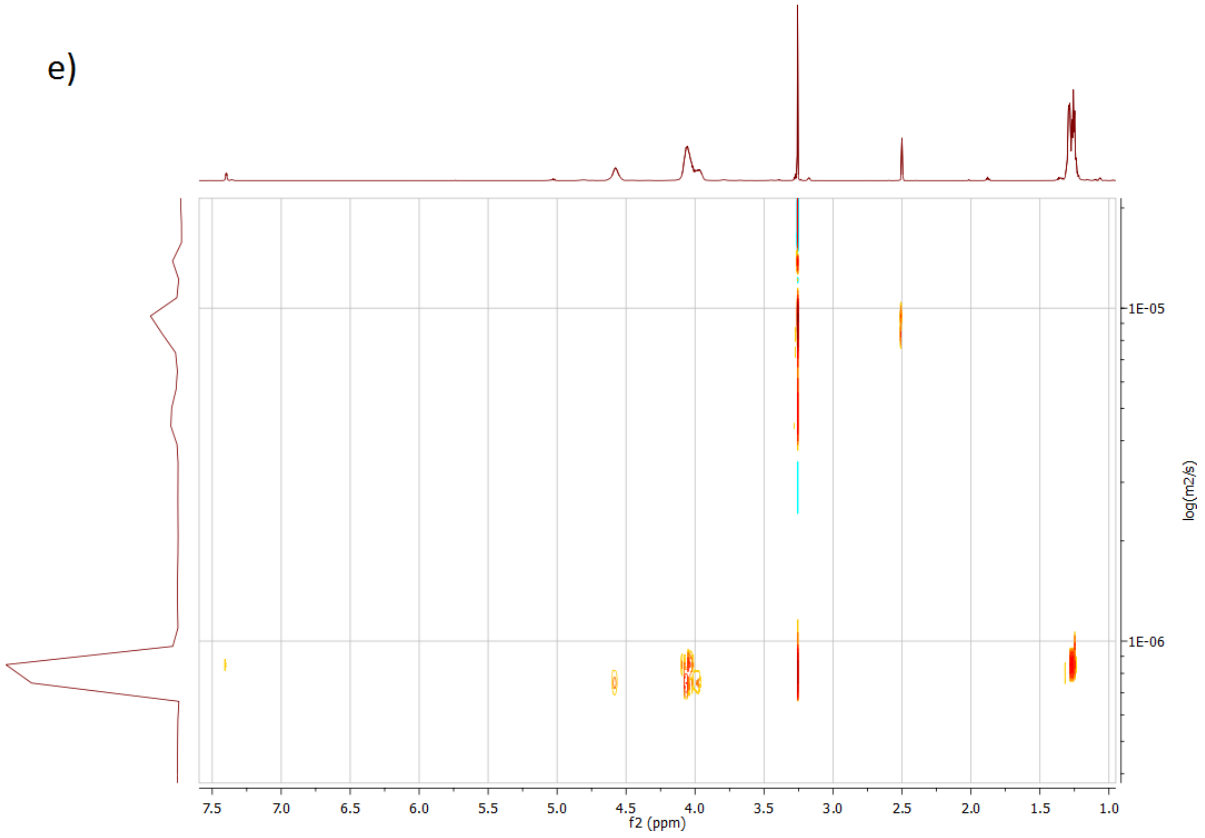

Fig. S11. ^{1}H DOSY of five representative examples in DMSO-d_6: a) $PEEP_{32}$, b) $P(EEP_{28}$-*co*-$EMEP_5)$; c) $P(EEP_{17}$-*co*-$EMEP_{16})$; d) $P(EEP_4$-*co*-$EMEP_{29})$; e) $PEMEP_{38}$. The diffusion coefficient calculated by Bayesian DOSY Transformation is for all copolymers in the same range.

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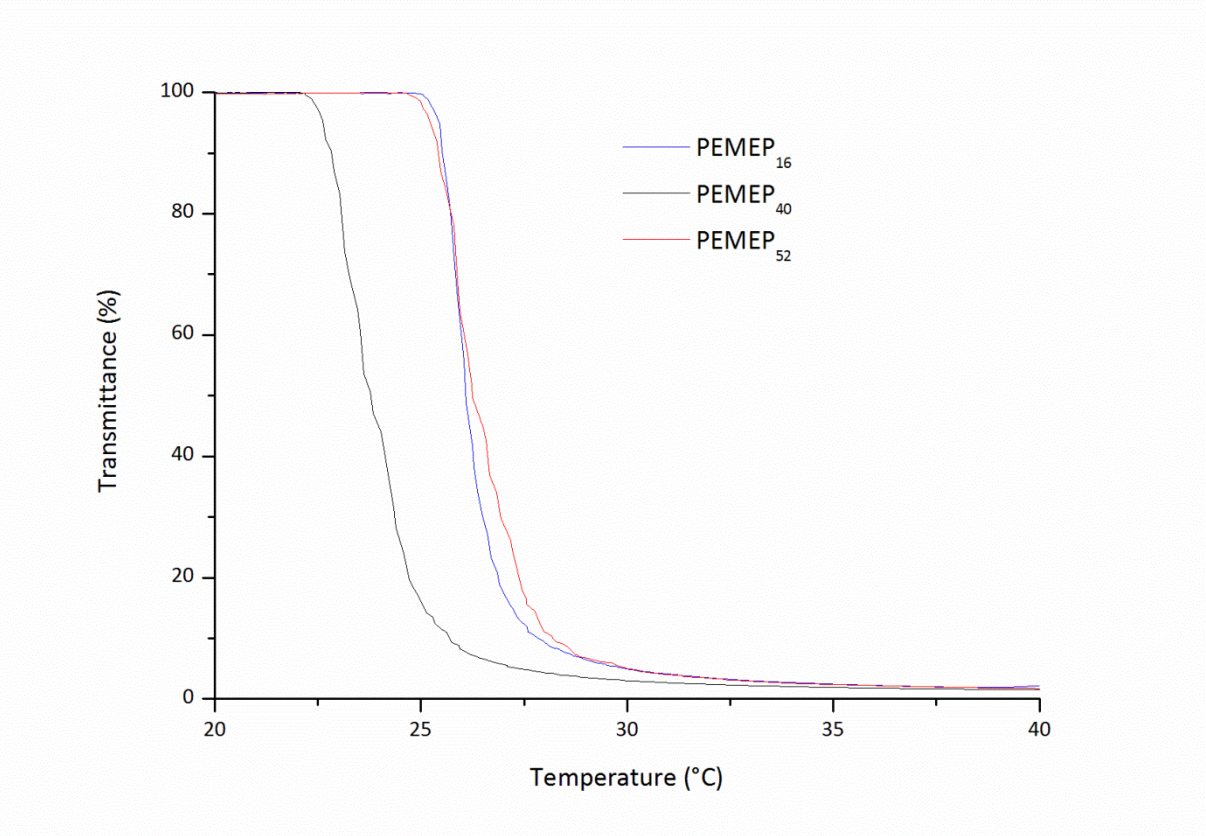

Fig. S12. Change in transmittance of PEMEP solutions with different molecular weights. Cloud points were determined in PBS pH 7.4 (10 mM) prepared from MilliQ water (18.2 mΩ) at a concentration of 10.0 mg·mL^{-1}. The heating/cooling rate was 1 °C·min^{-1} and values were recorded every 0.1 °C.

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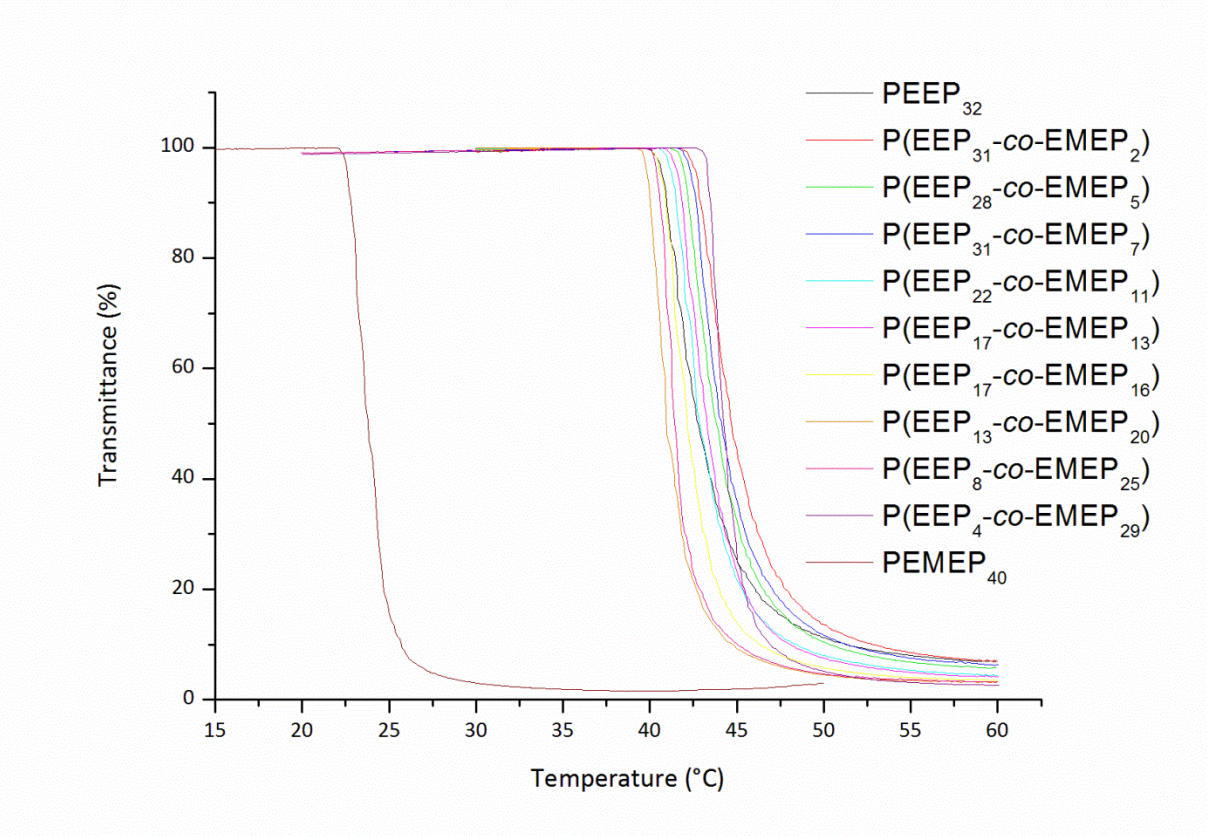

Fig. S13. Change in transmittance of P(EEP-*co*-EMEP) copolymers at a concentration of 10 $mg \cdot mL^{-1}$ in PBS pH 7.4 10 mM at 500 nm and a heating rate of $1°C \cdot min^{-1}$.