SUPPORTING INFORMATION

Influence of Amphiphilic Block Copolymer Induced Changes in Membrane Ion Conductance on the Reversal of Multidrug Resistance

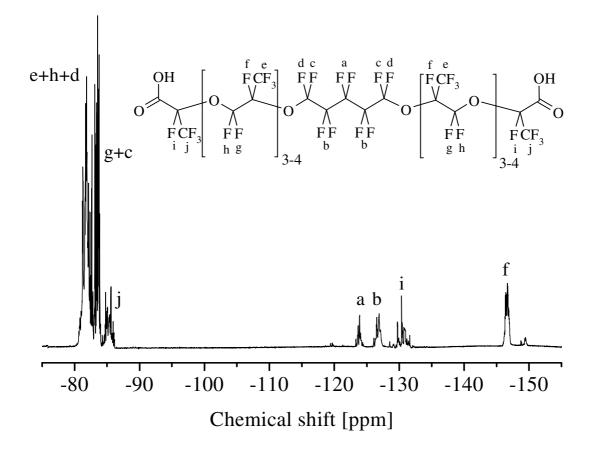
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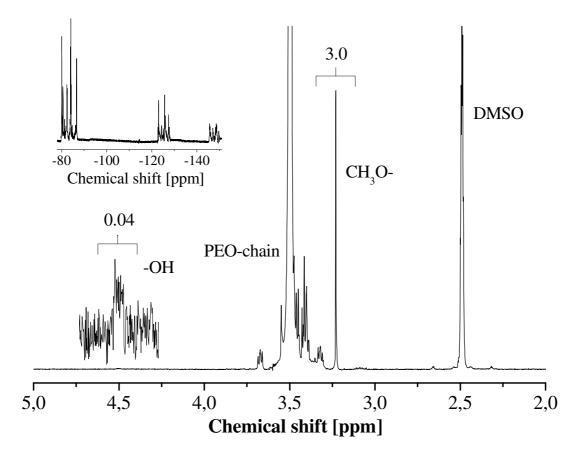
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Figure S1 shows the ¹⁹F NMR spectrum of PHFPO dicarboxylic acid with molar mass of 1500 g/mol.



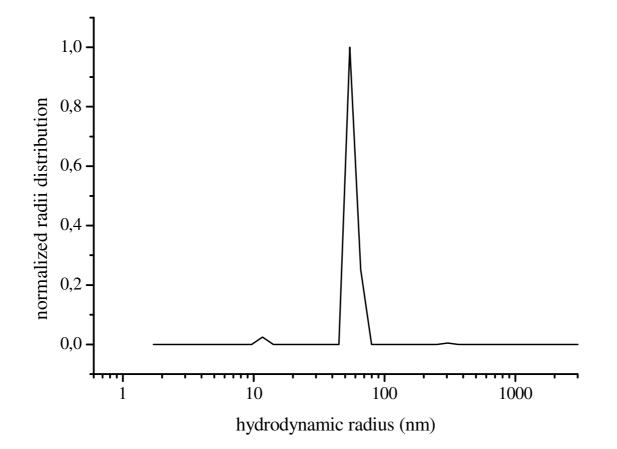
The 2F and 4F signals of the middle (a) and the two neighbouring (b) CF_2 groups from the initiator can be seen at -124 and -127 ppm, respectively. The signals of additional CF_2 groups (d and c) are located in the 35F multiplet between -81 and – 83 ppm. This signal comes also from the fluoromethyl group (e) and the fluoromethylene groups (g and h) of the PFHPO chain. The 7F signal of the CF groups (f) which belong to the PHFPO chain are in the range of -147 ppm. Additionally, the 6F signal of the fluoromethylene groups neighboring the carboxylic acid groups (j) at -85 ppm and the 2F signals of the CF groups (i) at -130 ppm can be identified.

Figure S2: ¹H-NMR spectrum of PEO-b-PHFPO-b-PEO dissolved in d⁶-DMSO. The inset shows the respective ¹⁹F-NMR spectrum.



The ¹H NMR spectra taken in d⁶-DMSO show the signals of the PEO chain between 3.3 and 3.6 ppm, which would also appear in non-converted PEO-MME. The triplet of the OH-protons of PEO-MME endgroup appears at 4.56 ppm and is drastically reduced. From the ratio of the integral of this peak and the integral of the 3H signal of methoxy protons at 3.24 ppm the conversion of PEO-MME to the respective block copolymers can be calculated¹. For the NMR spectrum under discussion the conversion is 96 %. The inset shows the respective ¹⁹F-NMR spectrum in d⁶-DMSO. A nearly complete disappearance of the signal at -130 ppm can be observed which belongs to the free PHFPO dicarboxylic acid (CF groups next to carboxylic acids groups, see discussion of Figure S1).

Figure S3. Normalized Radii distribution obtained by CONTIN fitting to Dynamic light scattering data of PEO-b-PHFPO-b-PEO in water using a polymer concentration of 1 wt.-%.



Due to the amphiphilic character of the block copolymers under investigation it was expected to find micellization in water where the hydrophobic perfluorinated blocks form the core and the corona is formed by PEO blocks.

REFERENCES

Dust, J. M.; Fang, Z. H.; Harris, J. M. Proton Nmr Characterization of Poly(Ethylene Glycols) and Derivatives. *Macromolecules* **1990**, *23* (16), 3742-3746.