

Supporting information

Tuning the Thermoresponsive Properties of PEG-Based Fluorinated Polymers and Stimuli Responsive Drug Release for Switchable ^{19}F Magnetic Resonance Imaging

Adil Usman,^{a,b} Cheng Zhang,^{a,b} Jiacheng Zhao,^{a,b} Hui Peng,^{a,b} Nyoman D. Kurniawan,^c Changkui Fu,^{a,b} David J. T. Hill,^{a,d} and Andrew K. Whittaker^{*a,b}

^aAustralian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, QLD 4072, Australia, ^bARC Centre of Excellence in Convergent Bio-Nano Science and Technology, The University of Queensland, St Lucia, QLD 4072, Australia, ^cCentre for Advanced Imaging, The University of Queensland, St Lucia, QLD 4072, Australia, ^dSchool of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia, QLD 4072, Australia.

Email: a.whittaker@uq.edu.au

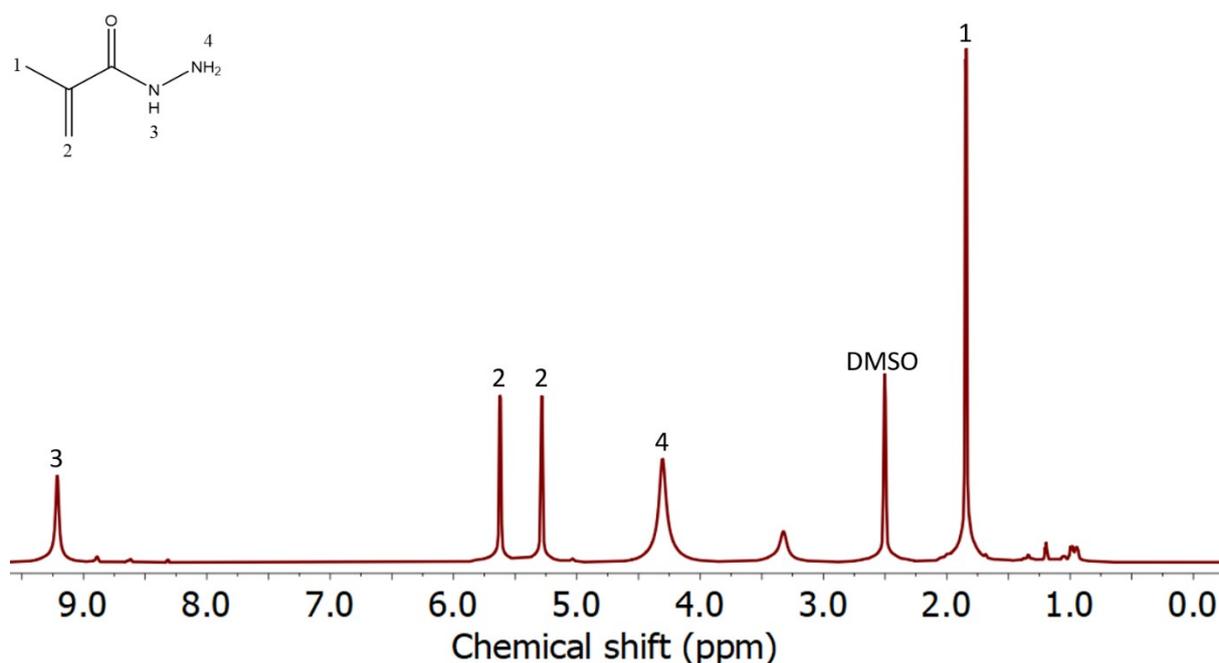


Figure S1 ^1H NMR spectrum of methacryloyl hydrazide monomer in DMSO.

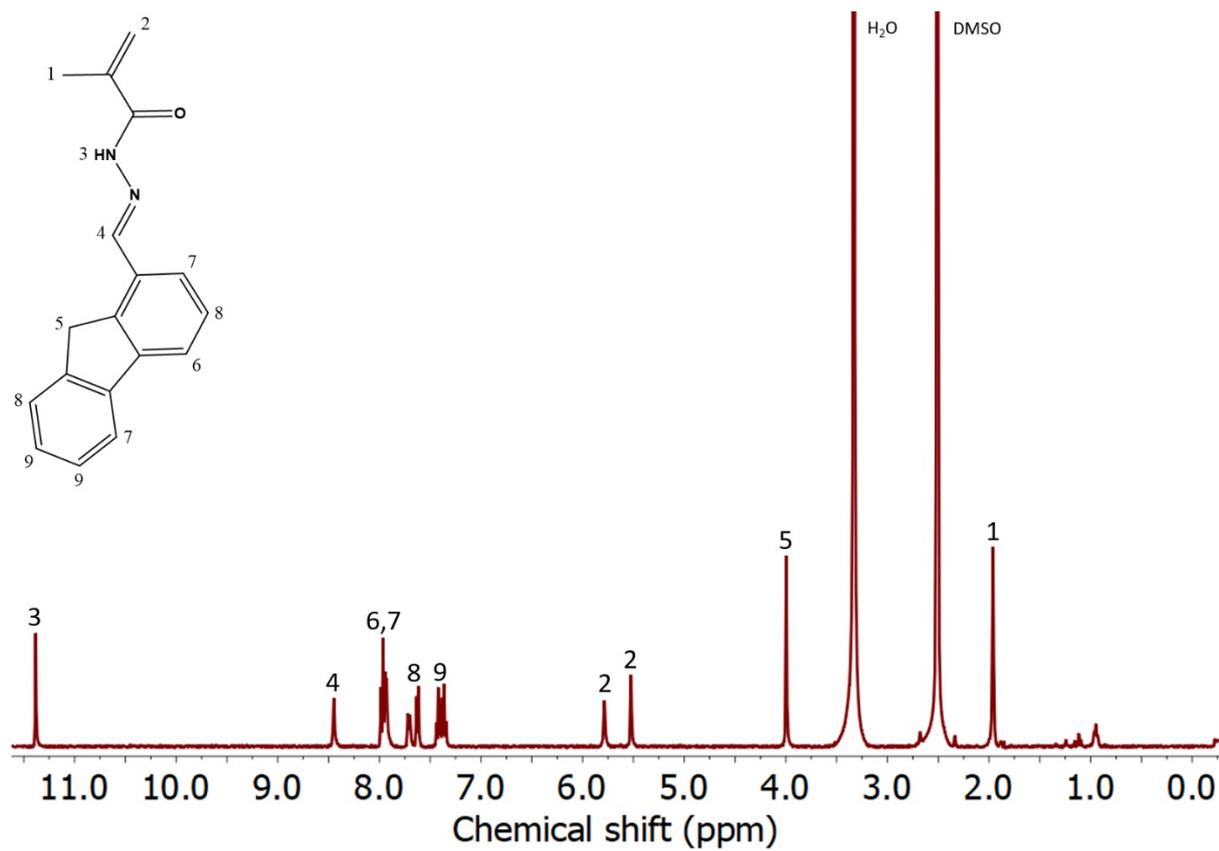


Figure S2 ¹H NMR spectrum of fluorene-2-carboxaldehyde conjugated hydrazide (DAH) monomer in DMSO.

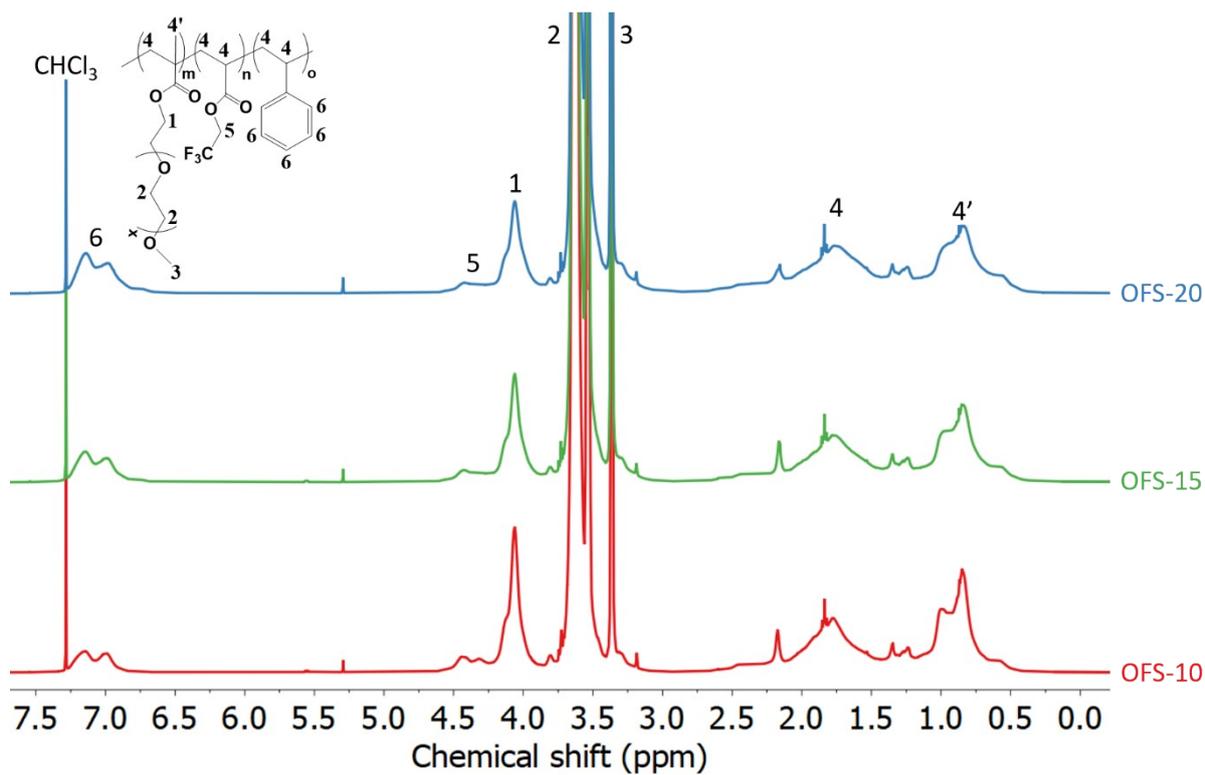


Figure S3 ^1H NMR spectra of OFS-10, 15 and 20 terpolymers and assignments to the peaks in CDCl_3 at 298 K.

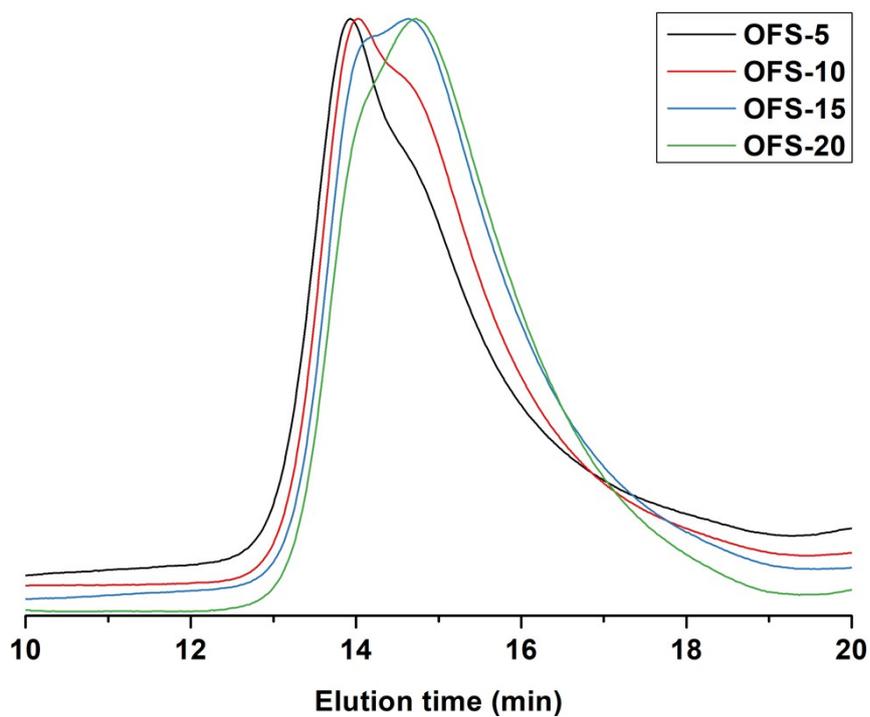


Figure S4 SEC curves of OFS terpolymers in THF.

Table S1 Tables representing the hydrodynamic diameters of OFS polymers in water as a

OFS-5	
Temp	d (nm)
298	12.46
301	12.78
303	12.85
305	13.09
307	13.72
309	14.81
311	17.23
313	1343
315	8656
317	9901
319	11970
321	13020
323	13340
325	13540

OFS-10	
Temp	d (nm)
298	10.73
301	10.89
303	11.22
305	11.74
307	13.03
309	3255
311	4090
313	9768
315	10220
317	11270
319	11790
321	12150

OFS-15	
Temp	d (nm)
296	9.766
298	11.31
300	11.39
302	18.66
304	1199
306	4595
308	6644
310	7386
312	9141
314	11170
316	11190

OFS-20	
Temp	d (nm)
293	11.29
295	165.5
297	191.6
299	223.4
301	3651
303	6794
305	8818
307	10030
309	13470
311	14320
313	15860

function of temperature.

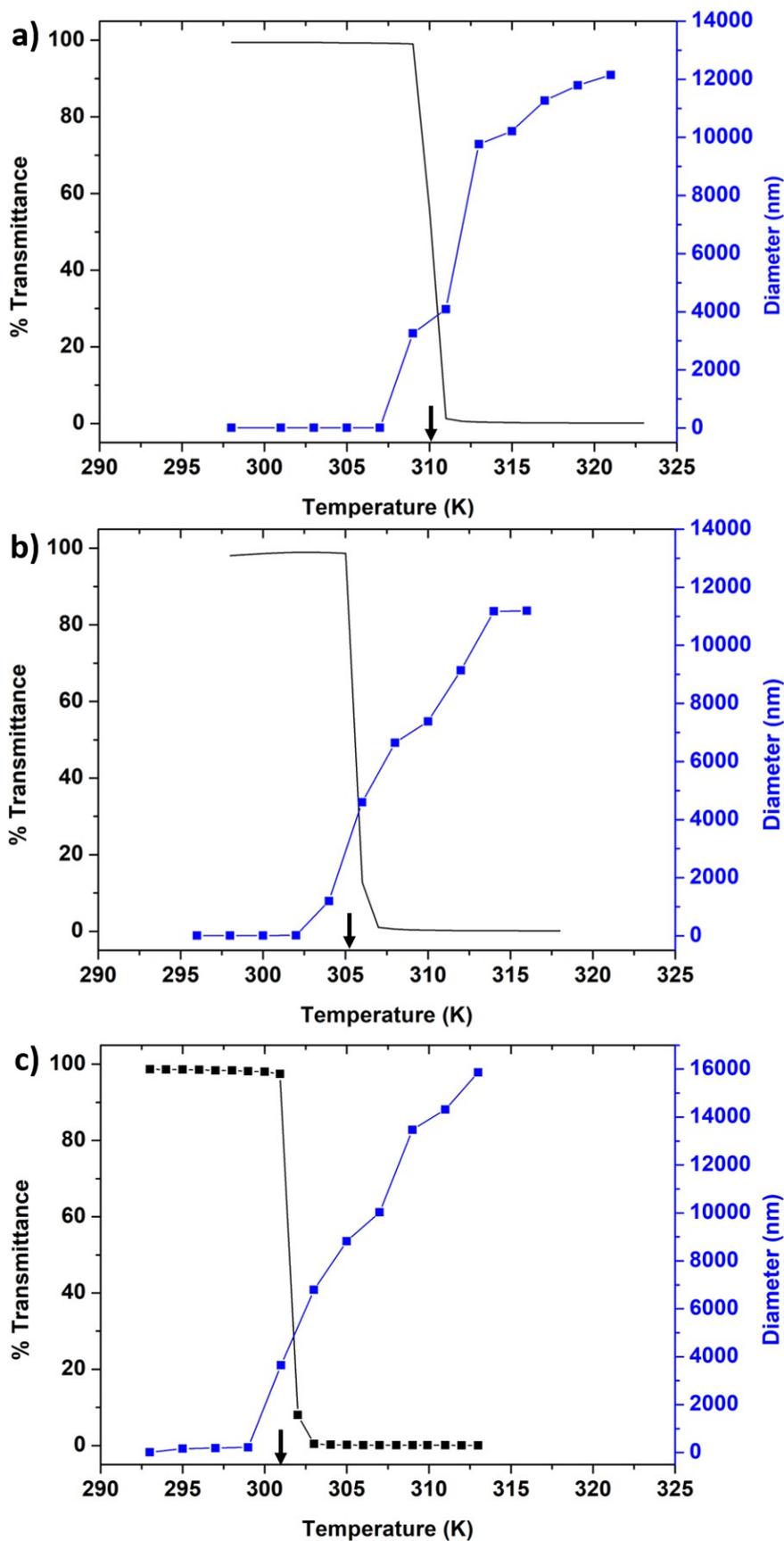


Figure S5 Hydrodynamic diameter of a) OFS-10, b) OFS-15 and c) OFS-20 in water as function of temperature. The arrows represent the LCST.

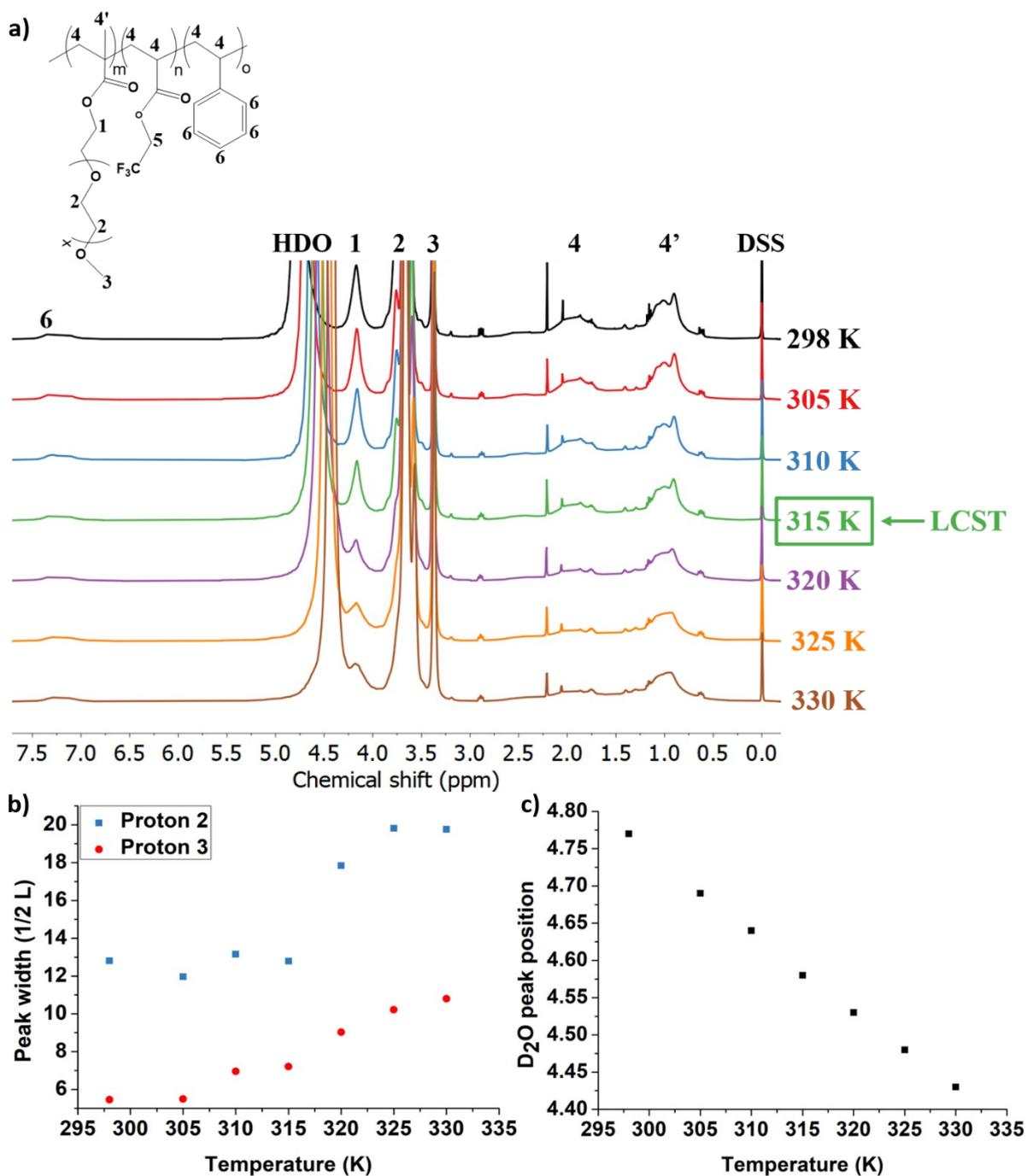


Figure S6 a) ^1H NMR spectra of OFS-5 terpolymer in D_2O b) plot representing increase in maximum width at half length for protons 3 and 2 and c) plot representing shifting of HDO peak at increasing temperature intervals from 298-330 K.

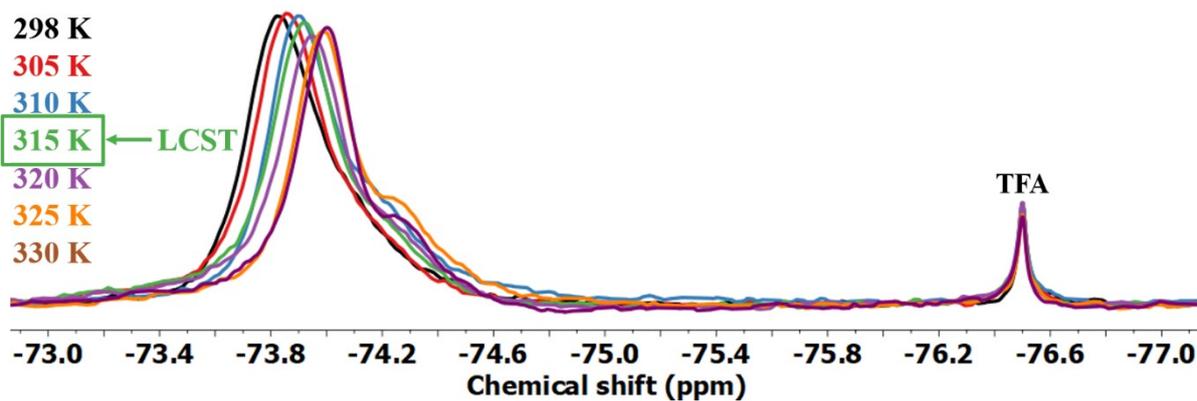


Figure S7 ^{19}F NMR spectra of OFS-5 terpolymer in D_2O at increasing temperature intervals from 298-330 K.

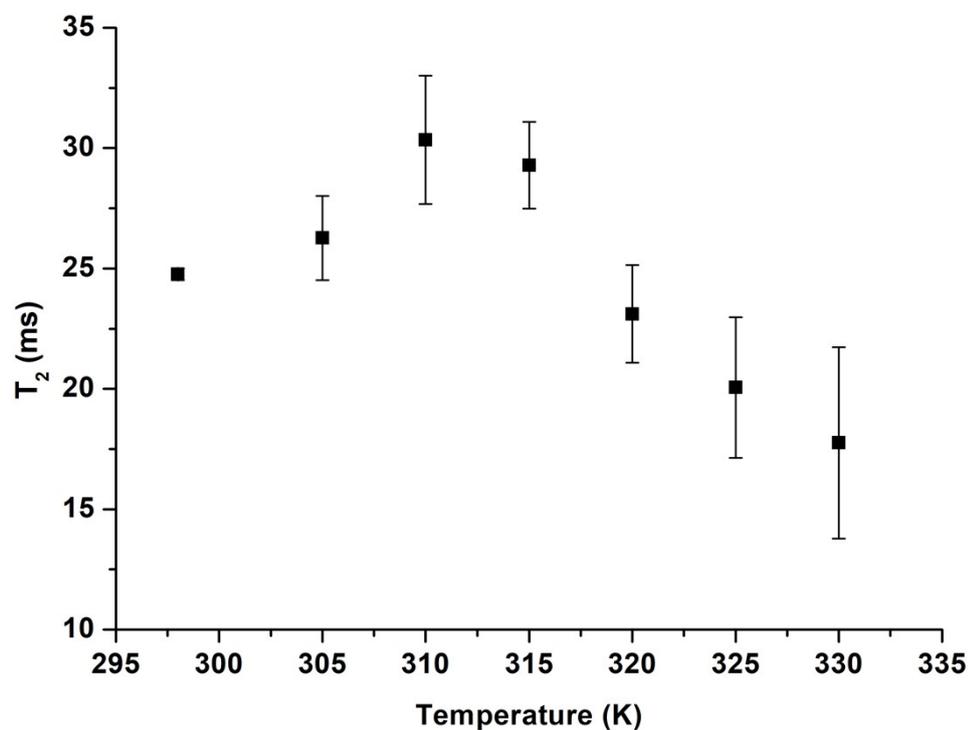


Figure S8 ^{19}F T_2 relaxation times versus temperature for OFS-5.

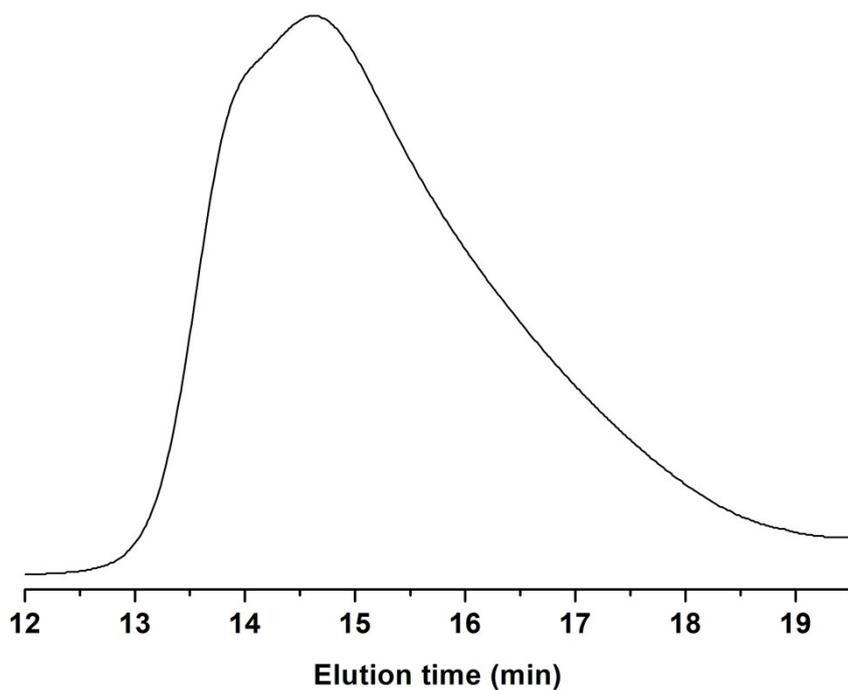


Figure S9 SEC curve of OFD terpolymer in THF.

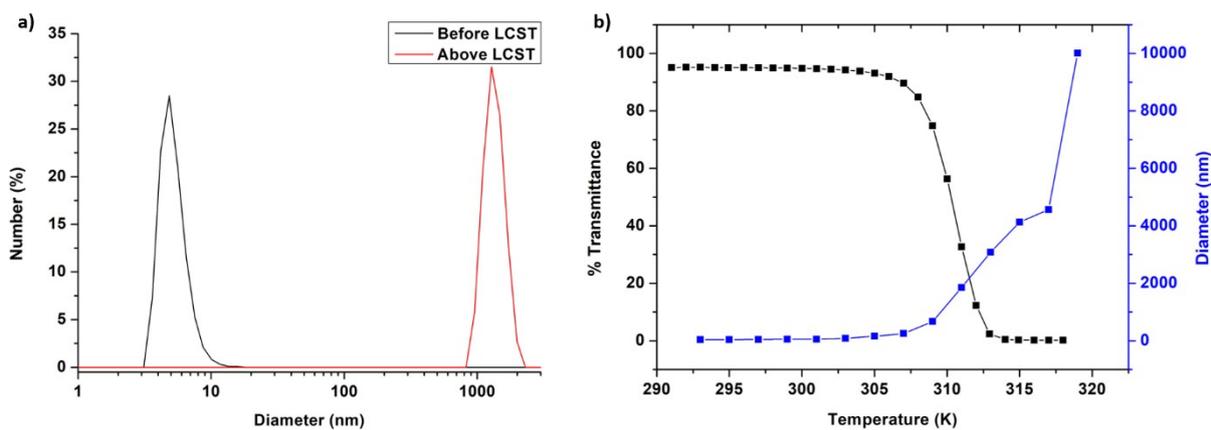


Figure S10 Number average hydrodynamic diameter of OFD terpolymer a) in water below and above the LCST and b) optical transmittance and hydrodynamic diameter plotted as function of temperature.

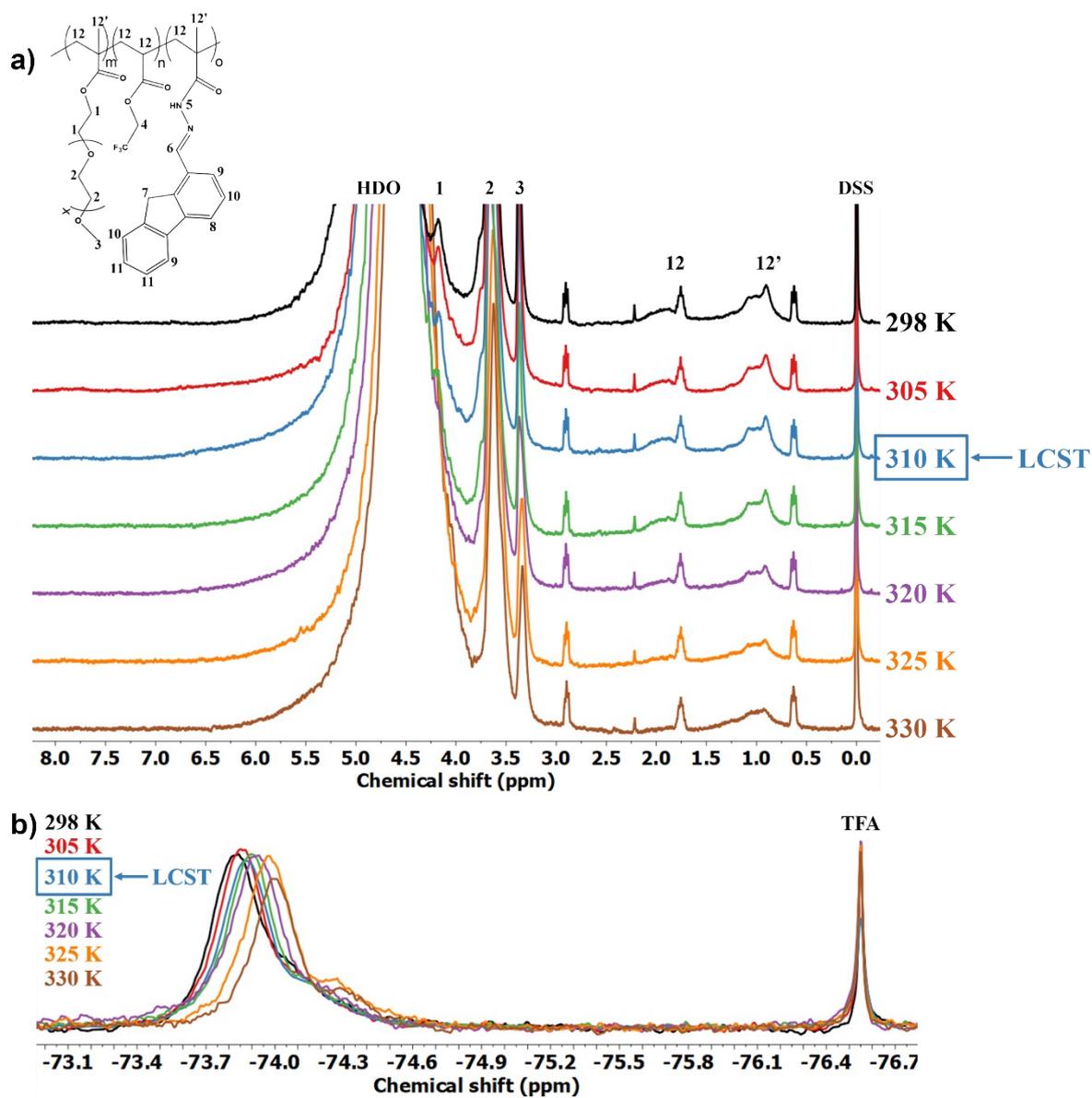


Figure S11 a) ^1H and b) ^{19}F NMR spectra of OFD terpolymer in D_2O at increasing temperature intervals from 298-330 K.

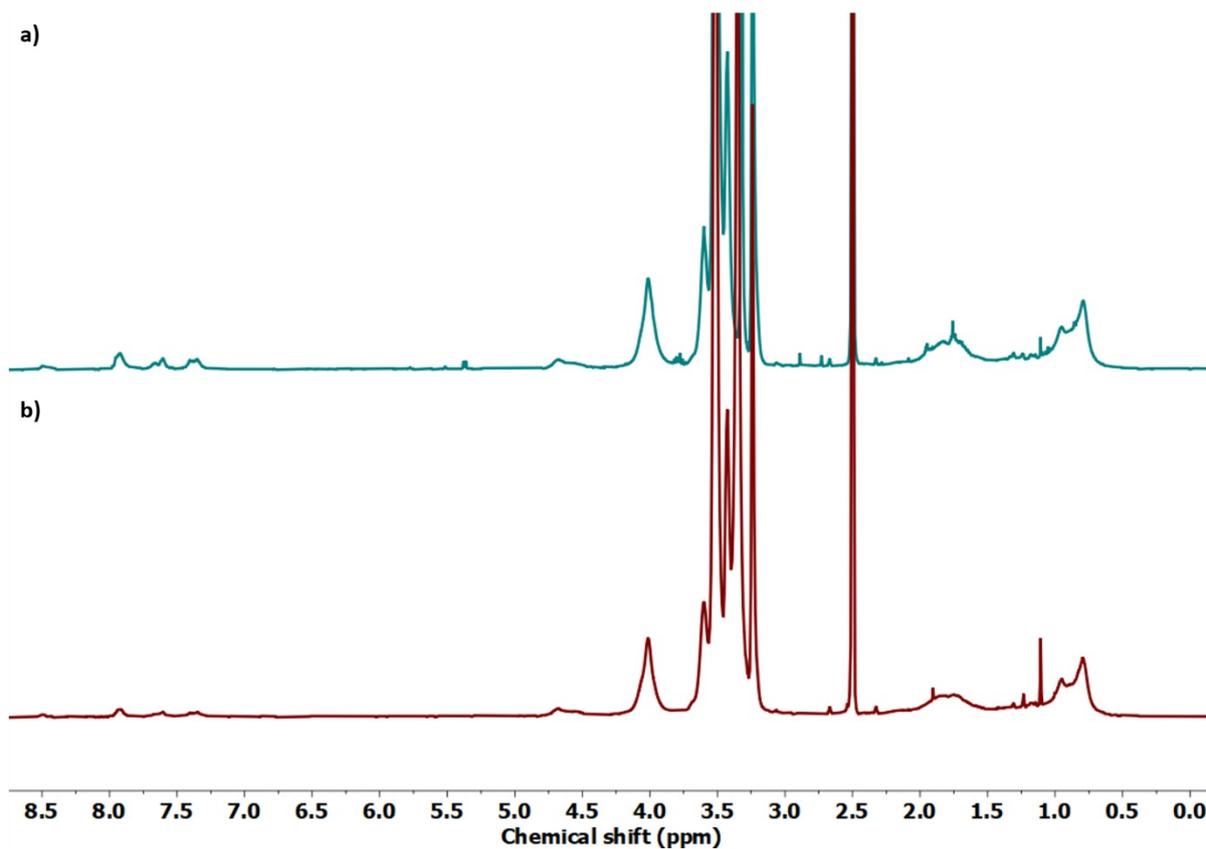


Figure S12 ^1H NMR spectra of OFD terpolymer in DMSO a) before and b) after drug release by hydrazone cleavage. The drug release is quantified by indexing the PEG peak at 4 ppm.

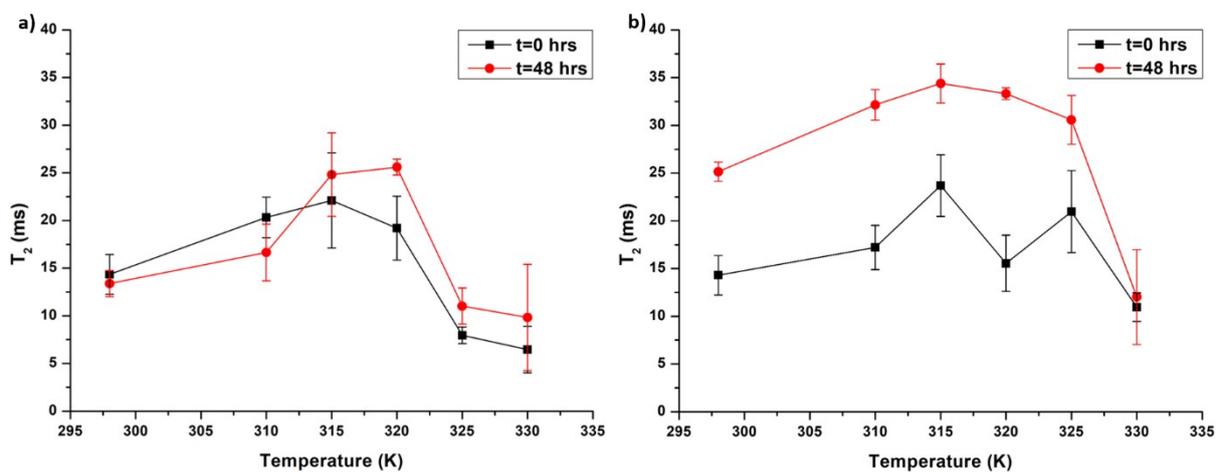


Figure S13 ^{19}F T_2 relaxation times of OFD terpolymer solutions in a) pH 7.4 and b) 5.5 PBS buffer before and after incubation at different temperatures.