Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Mechanism of the Formation of Microphase Separated Water Clusters in a Water - Mediated Physical Network of Perfluoropolyether Tetraol

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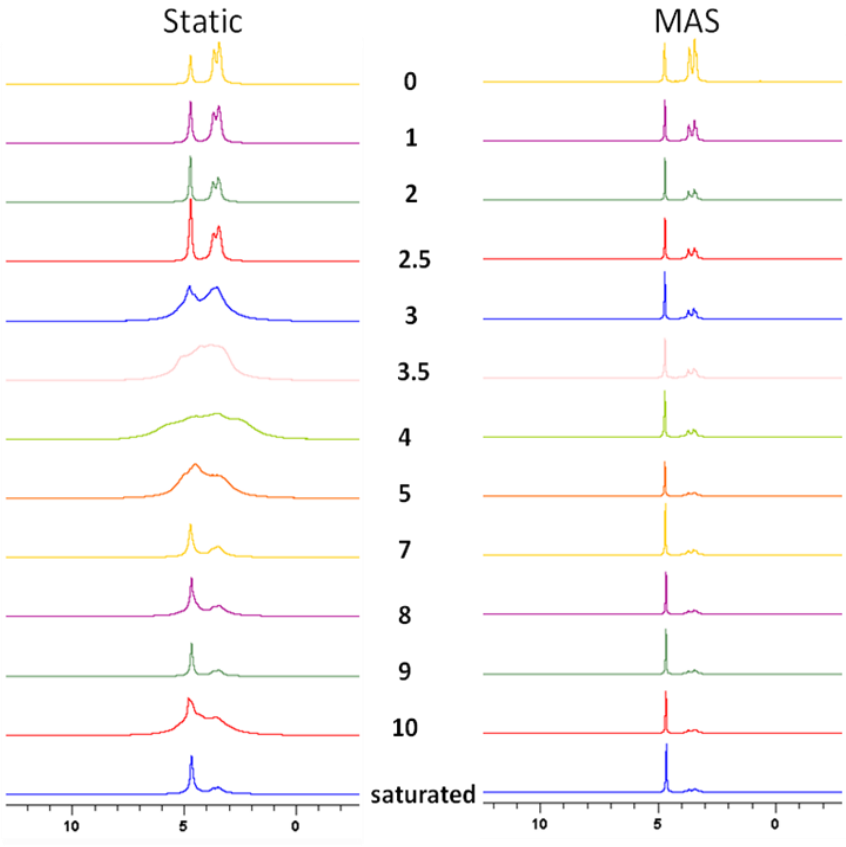
Table S-1: Composition of PFPE – tetraol: water samples

Entry No.	Sample Abbreviation	Water Content (Wt. %)
1	Neat	0
2	T+1	1
3	T+2	2
4	T+2.5	2.5
5	T+3	3
6	T+3.5	3.5
7	T+4	4
8	T+5	5
9	T+5.5	5.5
10	T+6	6
11	T+6.5	6.5
12	T+7	7
13	T+8	8
14	T+9	9
15	T+10	10
16	T+S	Saturated Tetraol Gel



(A) **(B)**

Figure S-1: ^{1}H static (A) and MAS (B) NMR spectra of PFPE tetraol samples. The top most plot is for the neat PFPE tetraol and the bottom one is that of equilibrium swollen PFPE tetraol gel in water. Hydration levels of samples prepared are 0, 1, 2, 2.5, 3, 3.5, 4, 5, 7, 8, 9, 10 wt. % and saturated.

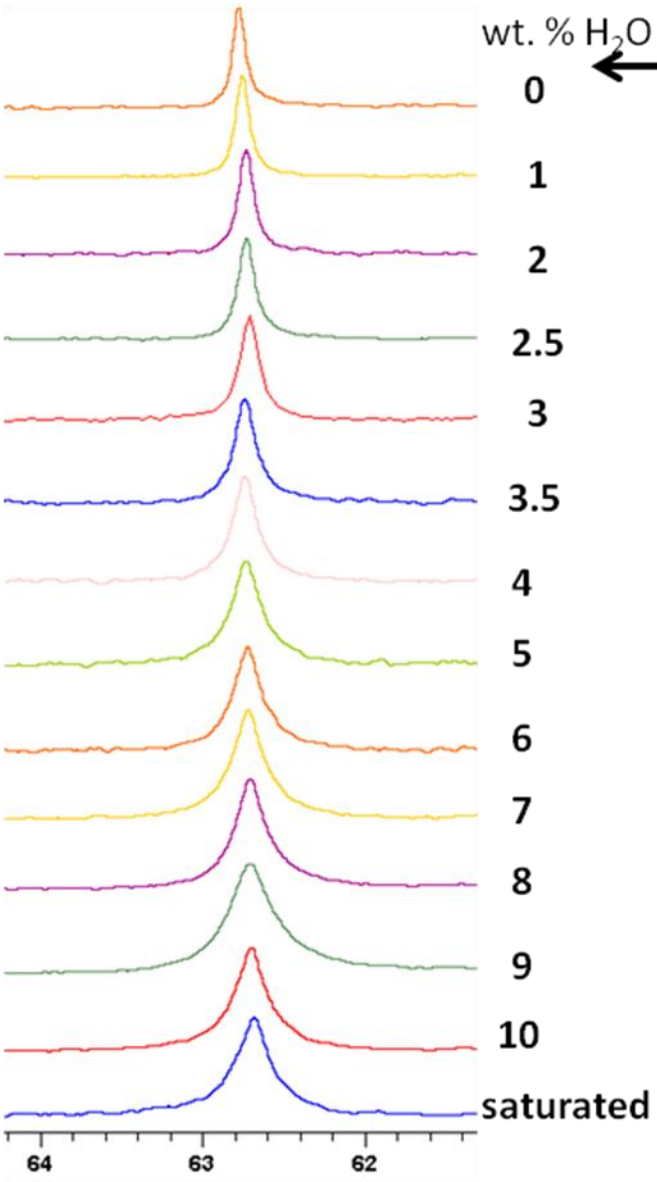


Figure S-2: ^{13}C HR MAS NMR spectra of PFPE tetraol samples. The top most plot is for the neat PFPE tetraol and the bottom one is that of equilibrium swollen PFPE tetraol gel. Hydration levels of samples are 0, 1, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, 10 wt. % and saturated.

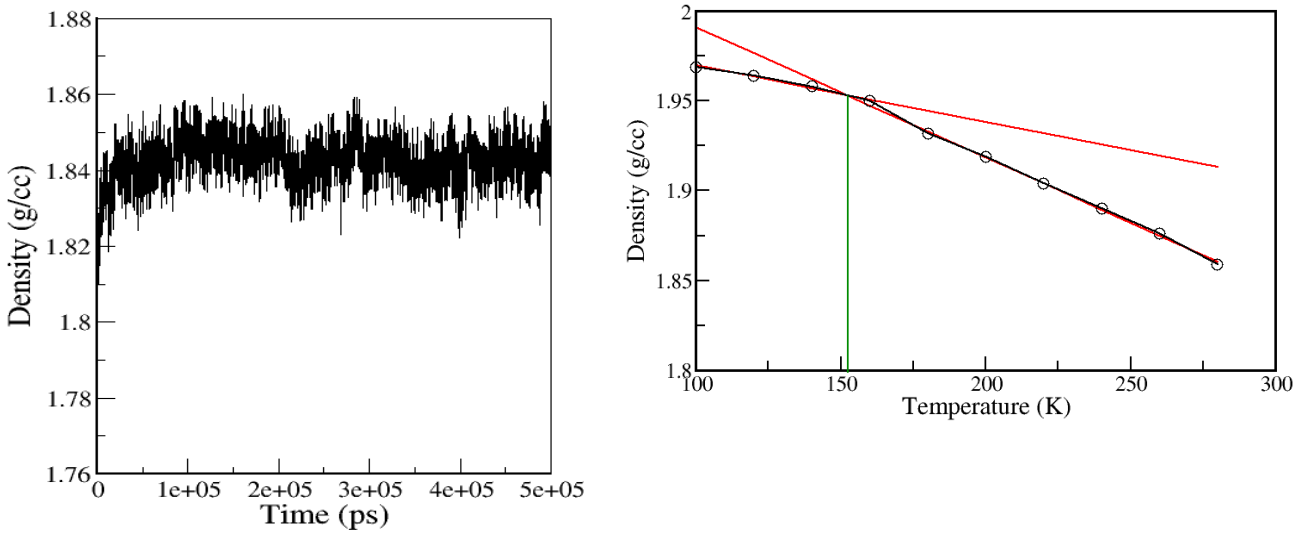
Table S-2: ^{1}H and ^{13}C NMR Spectral Assignments

	$OH\text{-}CH_2$	$\text{-}CH(OH)$	OCH_2	$Rf\text{-}CH_2$
^{1}H	3.58,3.48	3.80	3.56	3.75
^{13}C	62.9	70.7	73.4	70.7

1. Molecular dynamics simulations

1.1 Force field validation

The validation of force field for PFPE tetraol was done by calculation of density and glass transition temperature of the melt systems. The calculated density of polymer melt at 273 K and 1 atmosphere pressure was found to be 1.842 ± 0.003 g/cm^3 whereas experimental density of 1.84 g/cm^3 was reported[1]. The plot of density against time is shown in **Figure S-3a**. Therefore, density of the polymer system was well in agreement with the experimental data. For calculating the glass transition temperature, density was calculated at different temperatures ranging from 100 K to 300 K (starting well below the glass transition temperature up to well above the glass transition temperature) and plotted as a function of temperature in **Figure S-3b**. In **Figure S-3b**, it was observed that below 152 K the slope of the line which represents increase in density with decrease in temperature was less compared to that above 152 K. Therefore, the rate of change in density with temperature was different above and below this particular temperature. Hence, this particular temperature i.e. 152 K was the glass transition temperature for PFPE tetraol whereas the reported[1] experimental glass transition temperature is 163 K.



(a) **(b)**

Figure S-3: Density of PFPE tetraol a) as a function of time, b) as a function of temperature

Classical MD simulations were performed on bulk PFPE tetraol system as well as water solvated PFPE tetraol system at three different water content (3 wt. %, 5wt. % and 7wt. %) separately using all atomistic force field. Each polymer chain consists of 10 p block, 10 q block connected in alternate fashion and two terminal diol segments as shown in **Figure 1**. The molecular weight of the polymer chains used in MD simulations was 2115 g/mol which was same as polymers used in experiments. All the simulations were performed with GROMACS 4.6.3 code. For bulk as well as solvated tetraol system, simulations cell contains 350 polymer chains. Three solvated systems were prepared by adding (by randomly inserting with scaled Lenard-Jones (LJ) parameters for water oxygen) required amount of water molecules in the equilibrated bulk polymer system separately, so that the three systems contain 3 wt. %, 5 wt. % and 7 wt. % water, respectively.

Small NPT equilibration steps were performed by gradually scaling (up) the LJ sigma parameter of water oxygen. SPCE model[2] for water was used for solvated systems. In all the simulations, isobaric and isothermal (NPT) ensemble and periodic boundary conditions were used. V-rescale thermostat and Berendsen barostat were used for all the calculations and with long-range dispersion corrections as implemented in GROMACS. 1 μs production runs were performed for each system. NPT simulations of bulk tetraol were performed at different temperatures to find out the glass transition temperature to validate the force field. All the simulations were performed at 300 K (above the glass transition temperature of PFPE tetraol) for the melt system as well as the solvated systems. For all the systems, trajectories were recorded every 2 ps and last 10 ns of the production run were analyzed.

1.2 Cluster size analysis

Snapshots of the equilibrated PFPE tetraol bulk and PFPE tetraol: water systems with different concentrations of water are shown in **Figure S-4**.The sizes of the water clusters and their distributions were calculated as follows. The distance between the centers of masses (COM) among all the water molecules were first computed. All the water molecules for which the distance between the COMs came within 0.5 nm were considered to be the part of that particular cluster. This distance, 0.5 nm, was the distance of the second solvation shell of water molecule in pure water. The cluster sizes, i.e., the number of water molecules in a cluster, are calculated from each frame of the trajectory (last 10 ns of production run) separately for all the water solvated tetraol systems.

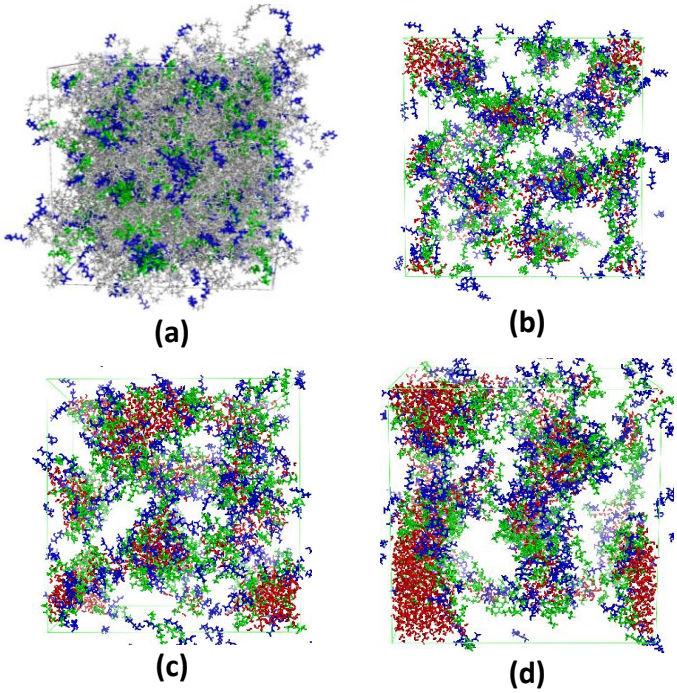


Figure S-4. Snapshots of PFPE tetraol a) bulk (Neat) b) 3 wt. % water c) 5 wt. % water and d) 7 wt. % water systems. Hydrophobic groups are not shown for clarity in b, c and d. Red: Water; Blue and green: hydrophilic terminal groups.

Finally, the number of occurrences of the cluster sizes, normalized by number of frames was plotted. Greater number of occurrences at a particular cluster size indicates higher probability of formation of cluster of that size.

We calculated the intra as well as inter molecular hydrogen bonding (H-bonding) between the hydrophilic end segments of the polymer chain (**Figure S-5a**) and the total H-bonds formed between water molecules and hydrophilic groups and within the hydrophilic segments (**Figure S-5b**) using the following two criterion: i) donor (in this case oxygen atom) is bonded to a hydrogen atom and if acceptor (another oxygen atom) is within 0.35 nm from the donor and ii) if the angle between the hydrogen-donor-acceptor is less than 30^0. **Figure S-5a** indicates that in polymer melt (black line), higher number of H-bonds are formed between the hydrophilic terminals compared to that in the hydrated systems. The addition of water molecules enables the formation of H-bonds between hydrophilic segments and water molecules. This increases the total H-bonds for the hydrated systems (red, green and blue lines, **Figure S-5b**). **Figure S-5b** reflects that the total numbers of H-bonds (considering both types of H-bonds) are much higher in hydrated polymer systems than in polymer melt. Therefore, a strong H-bonding network is formed in this system which facilitates the formation of gel; and as the hydration level increases, the H-bond network becomes stronger.

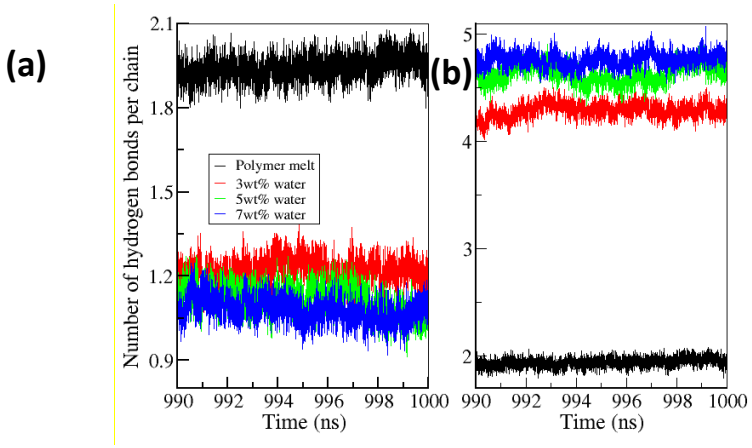


Figure S-5: **(a)** Number of hydrogen bonds formed between the terminal hydrophilic segments and **(b)** Number of hydrogen bonds of hydrophilic segments with itself and with water molecules.

We examined the effect of H-bonding network formation on the fluctuation of polymer chain. Since the diffusion of polymer chain in the well-structured network is very slow (in the order of 10^{-8} m^2/s), we determined root mean square fluctuation (RMSF) of all the monomer residues along the chain for polymer melt as well as for hydrated polymers (**Figure S-6a**). RMSF of a given monomer residue are calculated as a square root of the variance of the fluctuations around its average position. We estimated the RMSF of each residue and averaged it over all the polymer chains. The collections of atoms for each monomer residue are shown in (**Figure S-6b**). Two terminal residues (residue 1 (A) and residue 22 (D), **Figure S-6**) are the hydrophilic end terminals. The fluctuation of these terminal groups significantly decreases on addition of water molecules. Moreover, this reduction is observed for all the monomer residues of the chain (**Figure S-6a**). The inset of **Figure S-6a** shows the magnified RMSF plots of the hydrated systems. The results clearly indicate that as the hydration level increases, fluctuation of hydrophilic segments (residues 1 and 22) decreases.

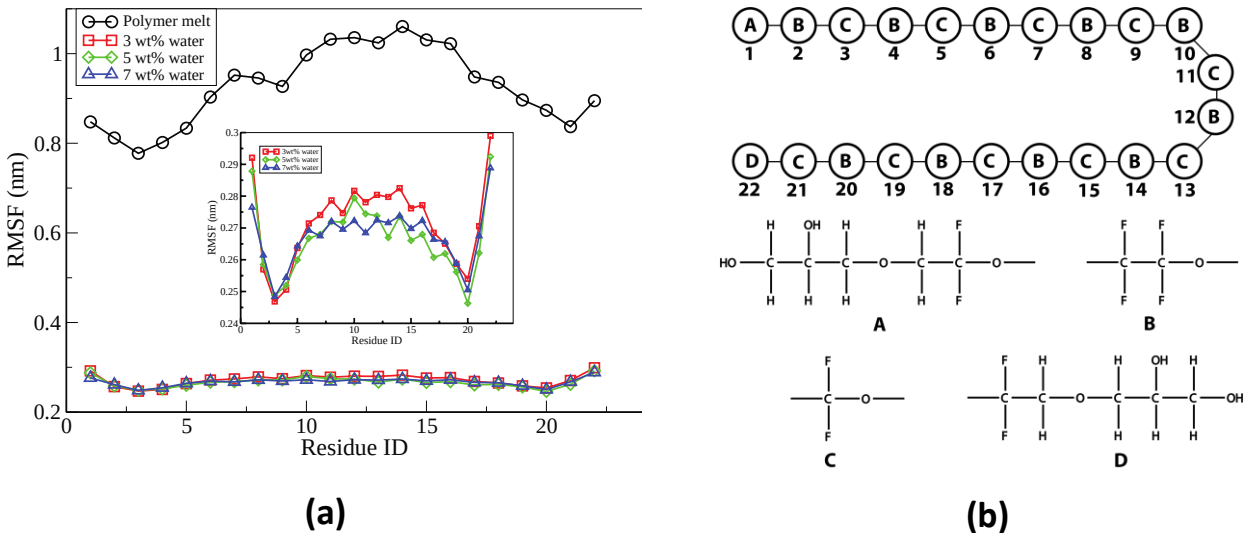


Figure S-6: (a) Root mean square fluctuation of all the residues along the polymer chain as a function of residue ID **(b)** A toy model of polymer chain (**Figure 1**) representing the residue IDs of (a)

2. NMR spectroscopy

High resolution magic angle spinning (HR-MAS) NMR experiments were performed on Bruker AV 500 MHz spectrometer equipped with a 4 mm HR-MAS probe. Small quantities of different tetraol samples prepared were transferred to a HR-MAS rotor containing spacers, which helps the samples to be placed at the center of the rotor. These samples were spun at a moderate spinning speed of 3 KHz. ^{1}H and ^{13}C NMR spectra of these samples along with the neat tetraol were recorded with standard pulse sequences and used for conventional high resolution NMR under static and MAS conditions. ^{1}H, ^{13}C and ^{19}F NMR studies of samples below 3 wt % hydration were also studied using conventional solution state NMR on a Bruker 400 MHz NMR spectrometer. ^{13}C T_2 measurements were performed on a Bruker Avance HD 700 MHz spectrometer using a 5 mm BBO probe.

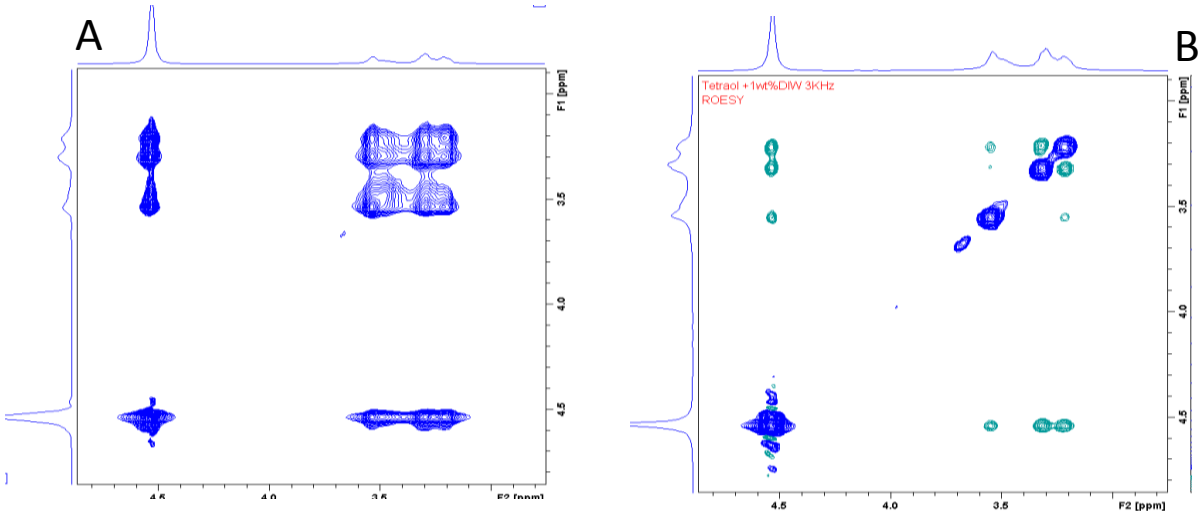


Figure S-7: ^{1}H HRMAS NOESY (A) and ROESY (B) spectrum of a 1 wt % hydrated PFPE tetraol sample. The spinning speed employed was 3 KHz and a mixing time of 250 msec and 125 msec were used for NOESY and ROESY measurements, respectively.

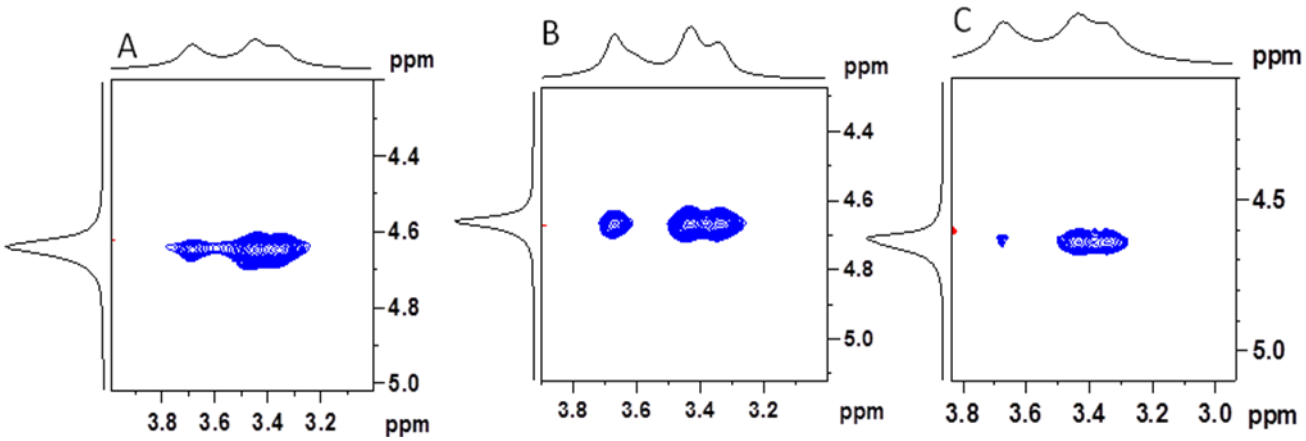


Figure S-8: ^{1}H HRMAS ROESY spectrum of PFPE tetraol gels: (A) 2 wt. % water, (B) 6.5 wt. % water and (C) saturated PFPE tetraol gel.

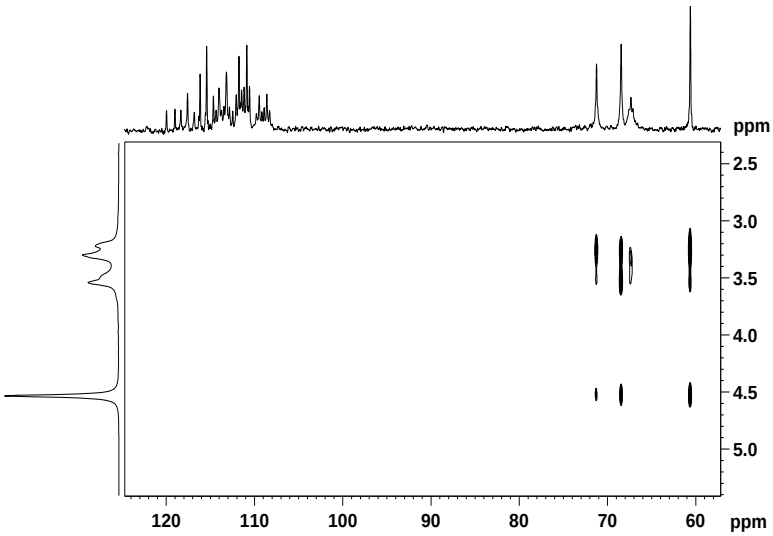


Figure S-9: ^{13}C-^{1}H HRMAS HOESY spectrum of 6.5 wt. % hydrated PFPE tetraol. Absence of cross peak between signal at 4.7 ppm (OH+H_2O) and the fluorinated carbons (105-120 ppm region) is noticeable.

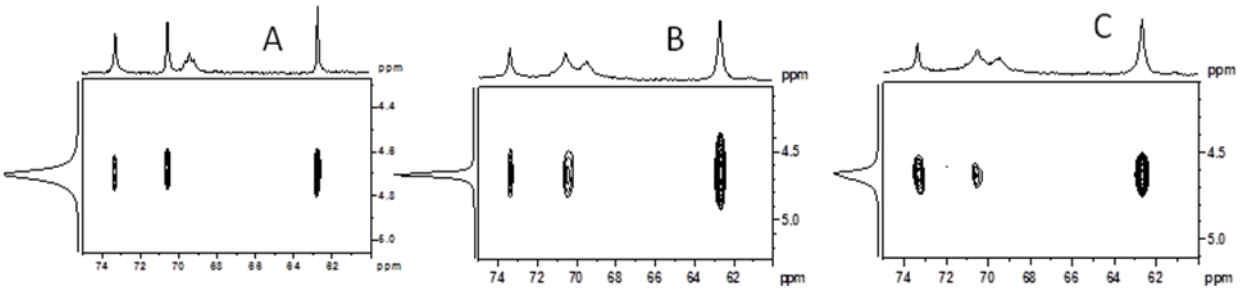


Figure S-10: Expanded ^{13}C-^{1}H HRMAS HOESY spectra of neat PFPE tetraol and PFPE tetraol gels: (A) neat, (B) 6.5 wt. % water and (C) saturated, highlighting the cross peak between carbons of terminal groups and proton signal at 4.7 ppm.

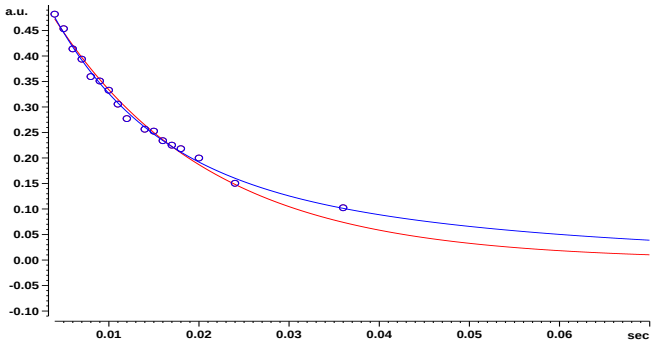


Figure S-11: T_2 decay curve of the signal at 70. 6 ppm of 3 wt. % hydrated sample with single component (red) and two components (blue) fit

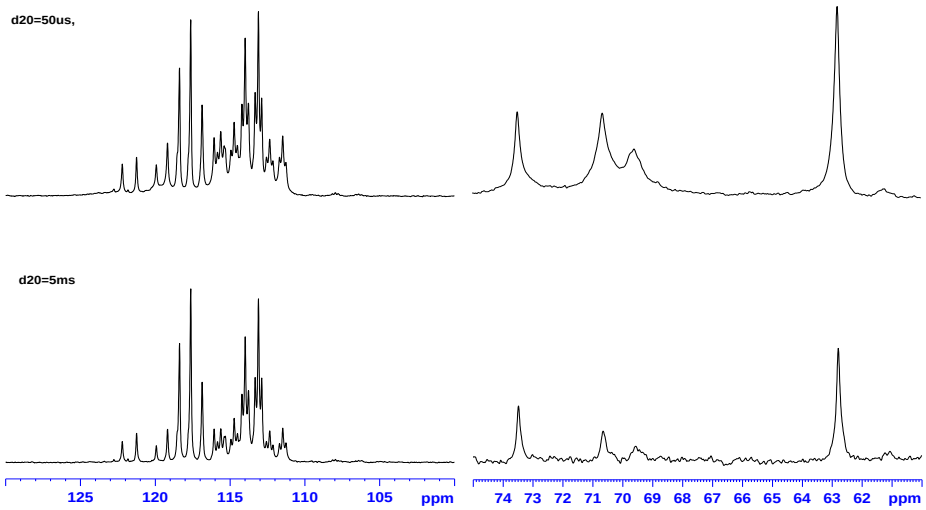


Figure S-12: Comparison of ^{13}C CPMG (Carr-Purcell-Meiboom-Gill) 1D spectra of hydrated PFPE (6.5 wt. %,) at two different refocusing times viz 50u sec (upper trace) and 5M sec (lower trace). This gives clear cut evidence for the two component T_2 behaviour. The spectrum obtained at the short refocusing time (50u sec) shows the presence of both the broad (short T_2) and "narrow" (longer T_2) components. The broad component is completely absent in the spectrum taken at higher refocusing time of 5 Msec.

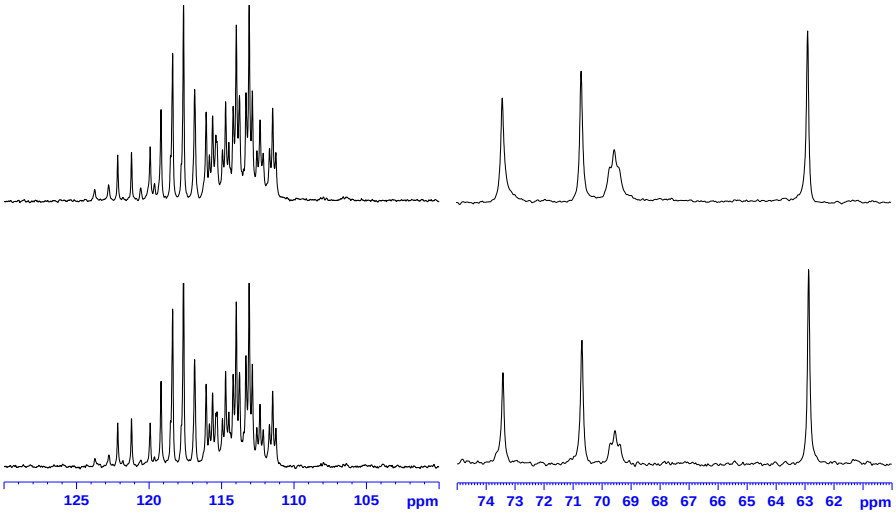


Figure S-13: Comparison of ^{13}C CPMG spectra of neat PFPE tetraol at two different refocusing times 50 us (top) and 5msec (bottom). The CPMG spectra taken at the two refocusing time intervals for the neat sample did not show any observable changes in the line width and only the expected decrease in intensity due to T_2 decay is seen.

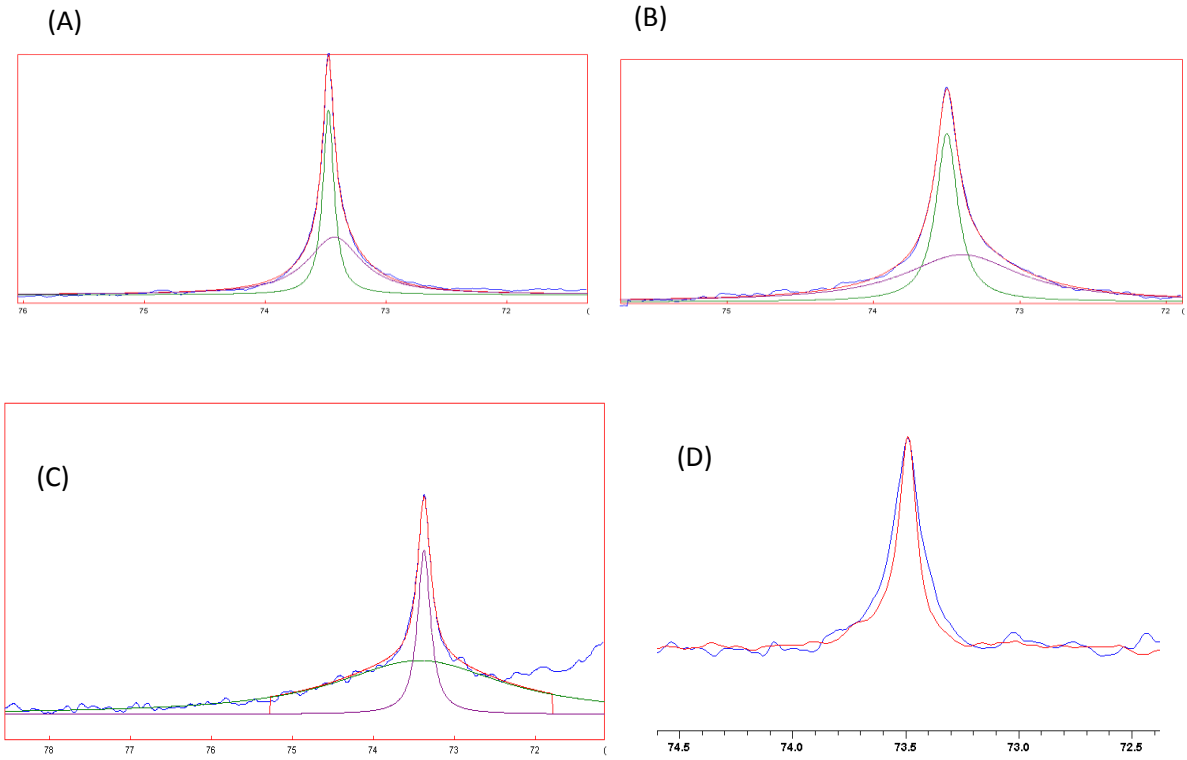


Figure S-14: Line shape analysis of signal at ~ 73.5 ppm for (A) 3 wt. % hydrated sample, (B) 6.5 wt % hydrated sample (C) saturated sample (D) Comparison of the line shape of the T_2 weighted (5 Msec) signal at 73.5 ppm of neat (red) and 6.5 wt. % hydrated (blue) sample.

Table S-3: Details of line shape analysis by DMFIT of hydrated PFPE samples

Sample	**Line**	**Amplitude**	**Position ppm**	**Width ppm**	**g/l ratio***	**T_2 ms**	**% Integral**
PFPE tetraol + 3 wt % H_2O	1	95.26	73.48	0.11	0.00	16.20	39.38
	2	30.22	73.43	0.54	0.00	3.34	60.62
PFPE tetraol + 6.5 wt % H_2O	1	38.34	73.50	0.18	0.00	10.06	40.20
	2	10.70	73.39	0.96	0.00	1.89	59.80
PFPE tetraol saturated gel	1	86.74	73.38	0.19	0.00	13.16	18.97
	2	28.37	73.43	2.51	0.00	1.01	81.03

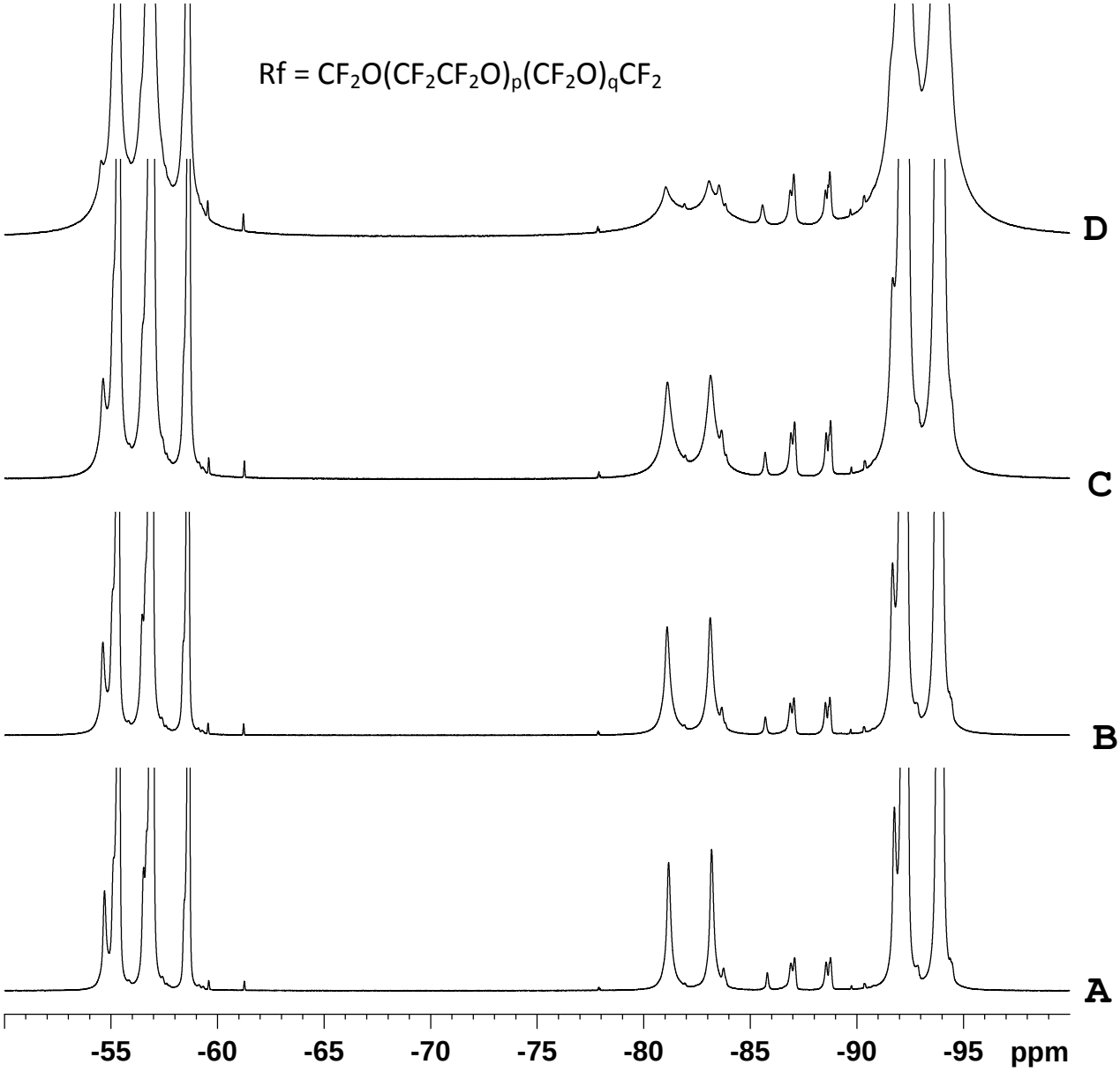


Figure S-15: Comparison of ^{19}F NMR spectra of PFPE tetraol: (A) neat PFPE tetraol, (B) 1 wt. % water (C) 2.5 wt. % water and (D) 6.5 wt. % water. Peaks in the region -80 to -83 ppm are assigned to the $-OCF_2$ groups closer to the terminal hydroxyl groups.[3]

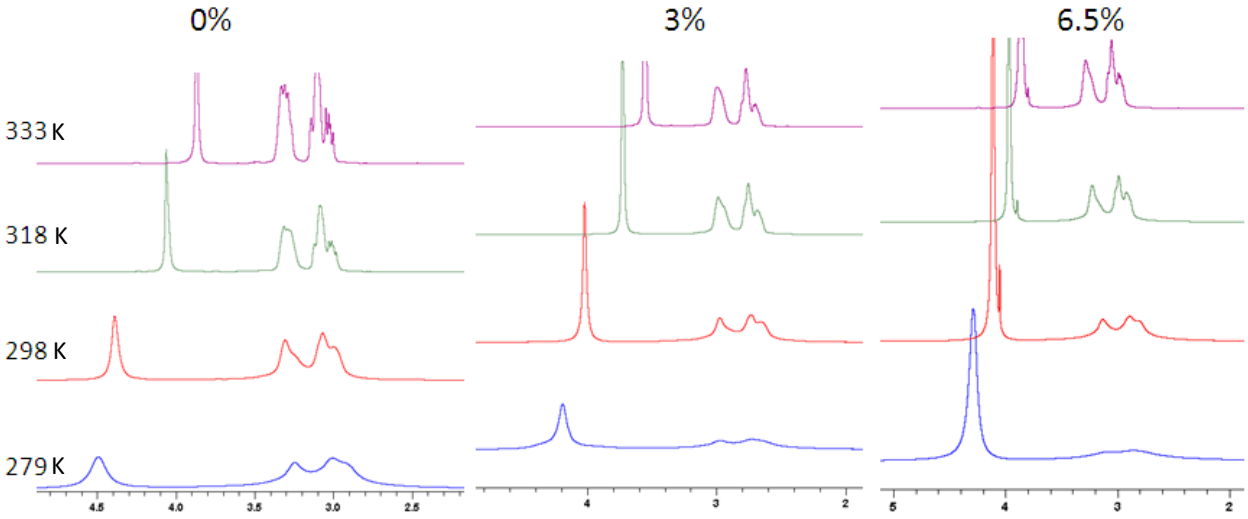


Figure S-16: Comparison of the ^{1}H NMR spectra of the end group signals of neat, 3 wt % and 6.5 wt % hydrated sample at different temperatures as indicated.

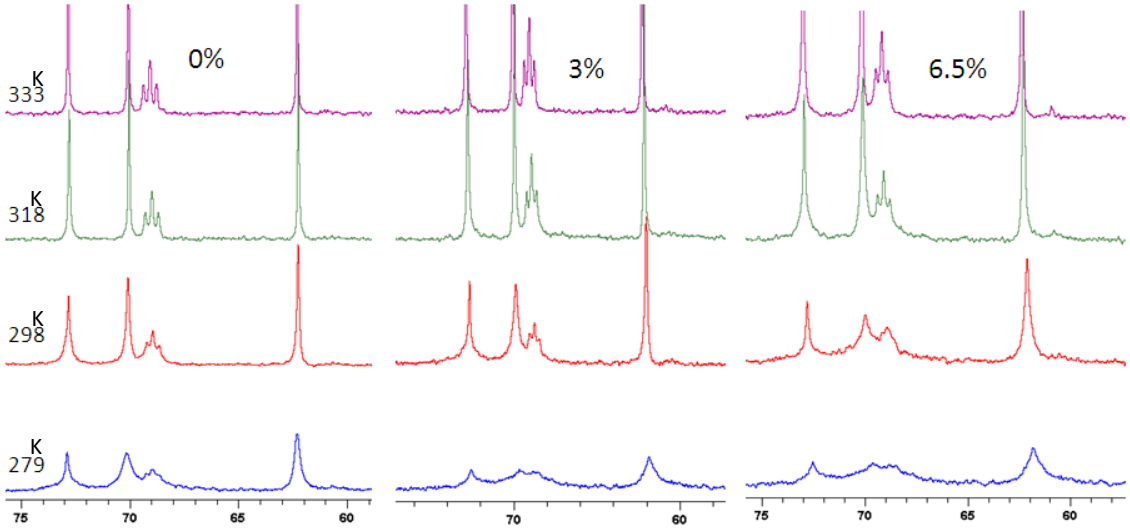


Figure S-17: Comparison of the ^{13}C NMR spectra of the end group signals of neat, 3 wt % and 6.5 wt % hydrated sample at different temperatures as indicated.

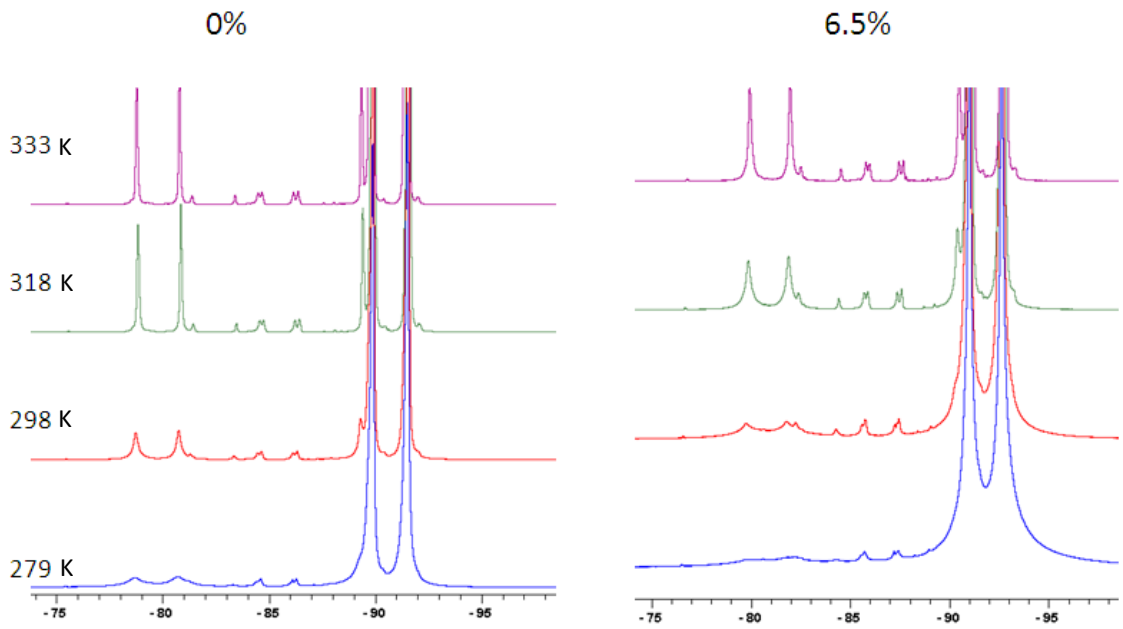


Figure S-18: Comparison of the ^{19}F NMR spectra (-75 to -95 ppm region) of the end group signals of neat PFPE tetraol and 6.5 wt % hydrated sample at different temperatures as indicated.

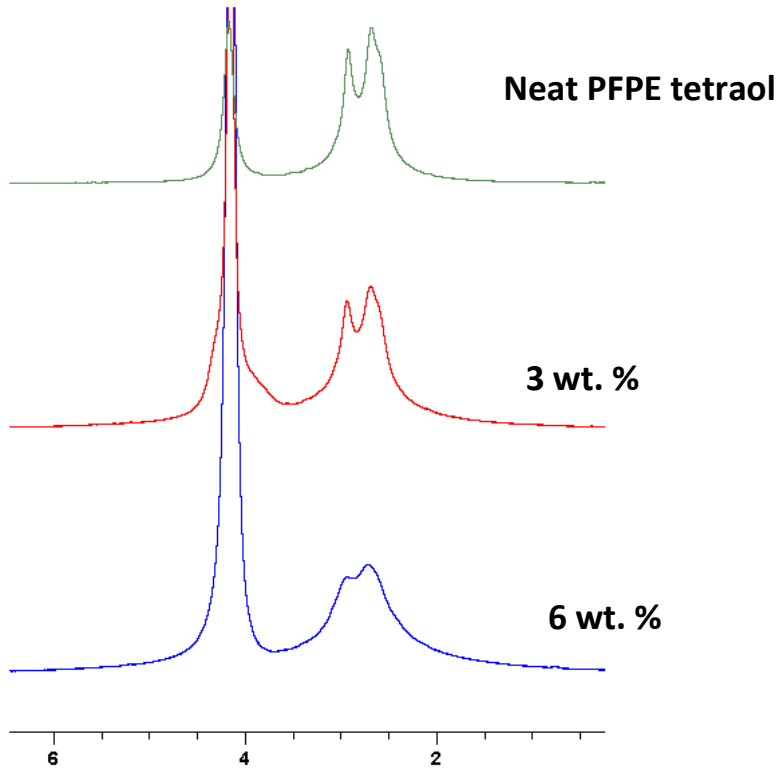


Figure S-19: Comparison of ^{1}H NMR spectra of neat, 3 wt % hydrated and 6.5 wt % hydrated sample at 279 K

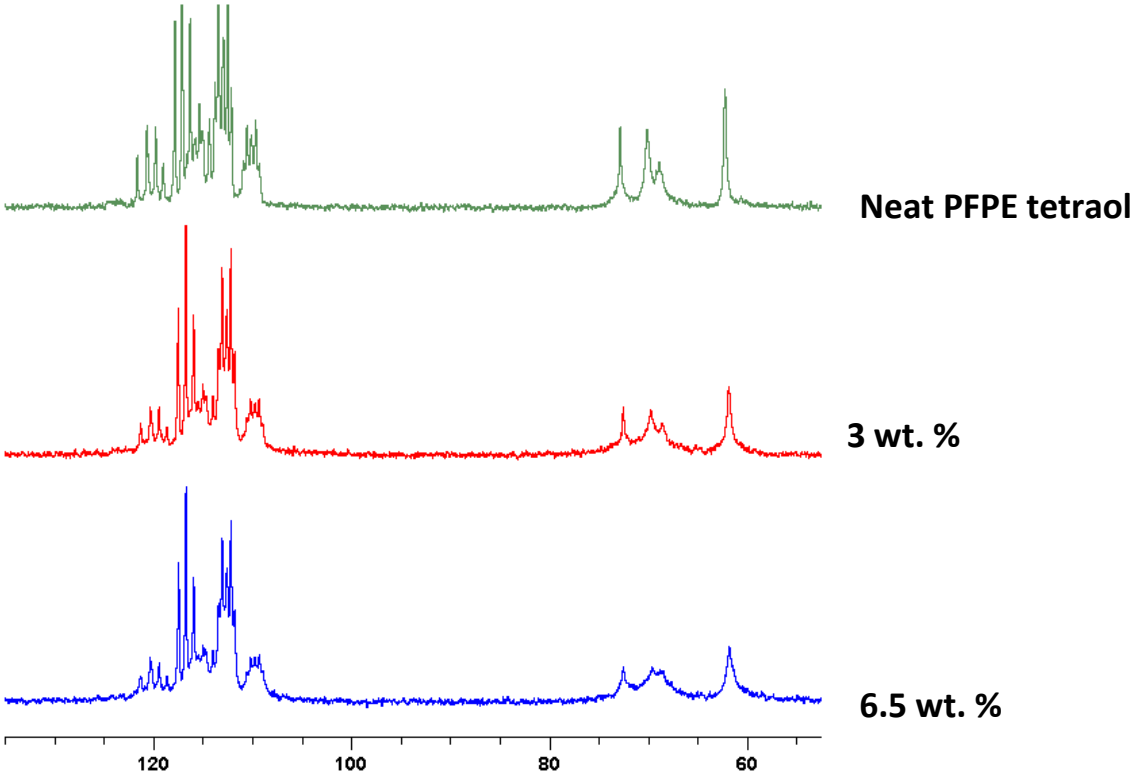


Figure S-20: Comparison of ^{13}C NMR spectra of neat, 3 wt % hydrated and 6.5 wt % hydrated sample at 279 K.

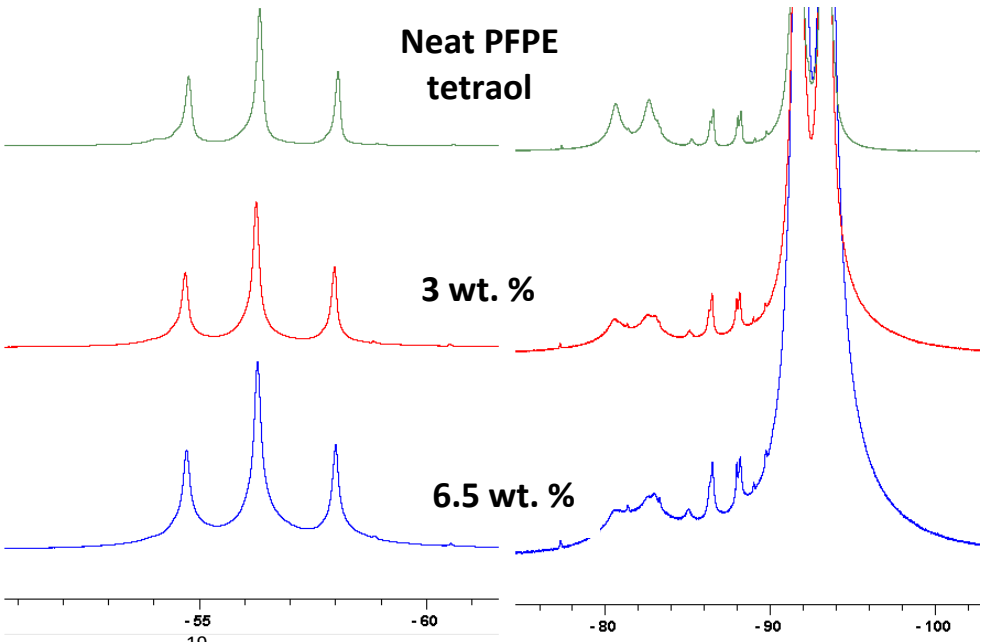


Figure S-21: Comparison of ^{19}F NMR spectra of neat, 3 wt % hydrated and 6.5 wt % hydrated sample at 279K

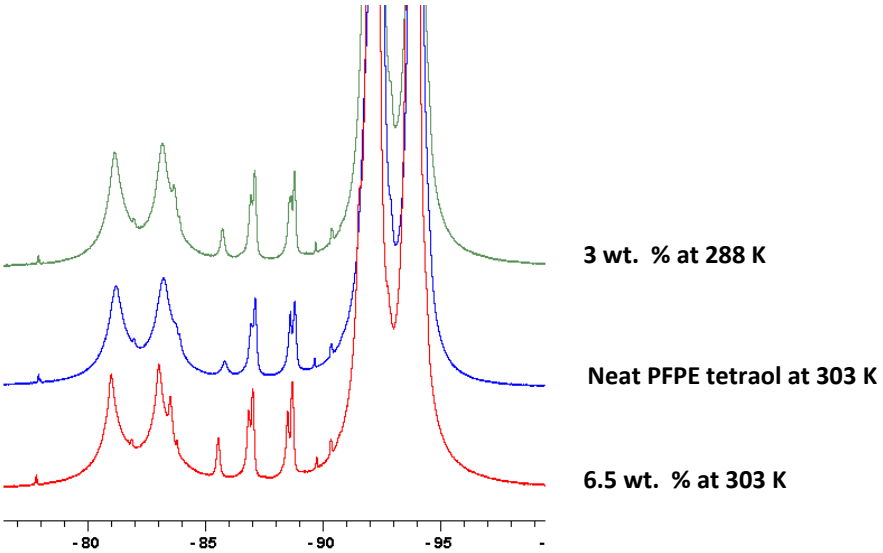


Figure S-22: ^{19}F NMR spectra of neat, 3 wt % hydrated and 6.5 wt % hydrated samples at indicated temperatures.

2.1 ^{13}C T_1 and T_2 measurements:

We feel that in the PFPE-water system under investigation, the gelation phenomenon is primarily driven by hydration of the hydrophilic end groups followed by intermolecular association of different hydrated PFPE molecules. Our NMR studies show that the hydration does not affect the line width of ^{13}C and ^{19}F resonances of the hydrophobic perfluoro moieties of PFPE. Only a few resonances probably closer to the hydrophilic ends (Attempts were not made for a complete assignment of all the carbon resonances) show observable broadening in the ^{19}F spectrum of the 6.5% hydrated sample (**Figure S-23**) and ^{13}C resonances of even the saturated gels (**Figure S-24**). On the contrary, the ^{13}C and ^{1}H resonances of end group moieties exhibited appreciable broadenings (**Figure S-25**). These observations seem to suggest that the gelation is due to association of the hydrophilic end groups rather than the one involving association of hydrophobic segments of PFPE. The hydrophobic association could have led to broadening of all the ^{19}F and ^{13}C resonances of PFPE instead of a few weak signals of them, as observed (**Figures S-23, 24**). In other words, the gelation does not seem to reduce the local dynamics of the hydrophobic part of the molecules. This observation is different from the aggregation phenomena observed for many of the bolaamphiphilic systems in which gelation is driven by hydrophobic association.

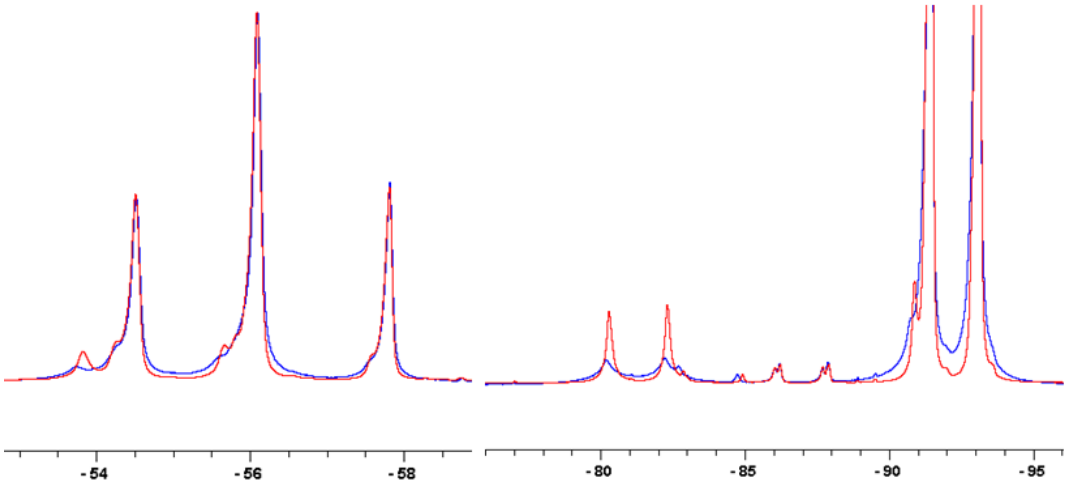


Figure S-23: Comparison of ^{1}H decoupled ^{19}F spectra neat (red) and 6.5% hydrated PFPE tetraol samples.

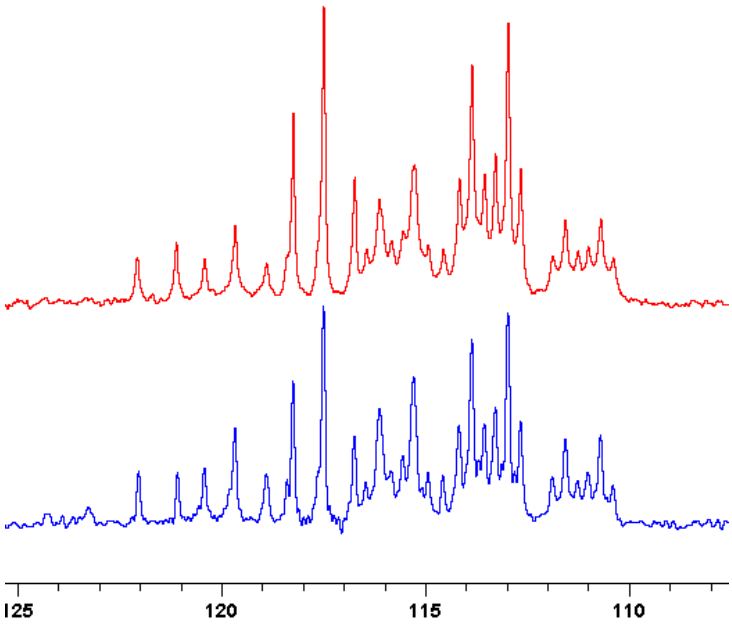


Figure S-24: Comparison of ^{1}H decoupled ^{13}C HRMAS spectra of the end group carbons of neat (blue) and saturated hydrogel (red) samples of PFPE tetraol).

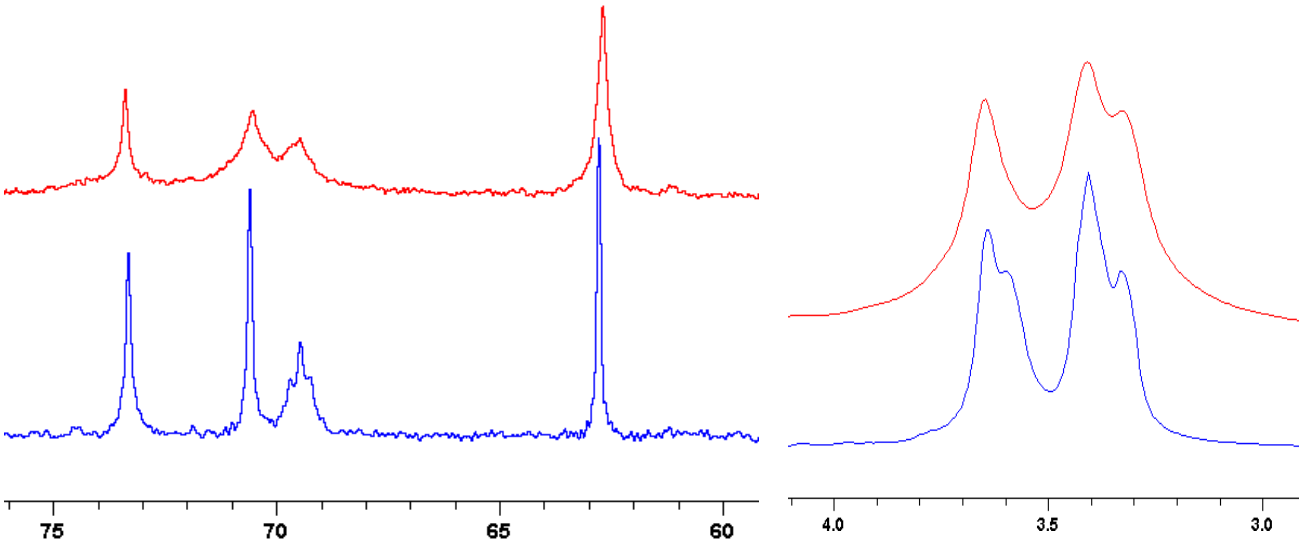


Figure S-25: Comparison of ^{1}H (right) and ^{13}C (left) HRMAS spectra of the end group protons and carbons of neat (blue) and a saturated hydrogel (red) samples of PFPE tetraol).

Independent ^{13}C T_1 and T_2 relaxation time measurements using standard pulse sequences on these systems using conventional high resolution NMR (700 MHz, 125 MHz for ^{13}C). ^{13}C spectrum is divided into different regions for estimation of T_1 as shown in **Figure S-26.** The region between 130 to 110 ppm is of fluorinated carbons. The signals in the 80 to 60 ppm region represented the end groups containing OH functions. Assignment of various carbons and protons are given in **Table S-2.**

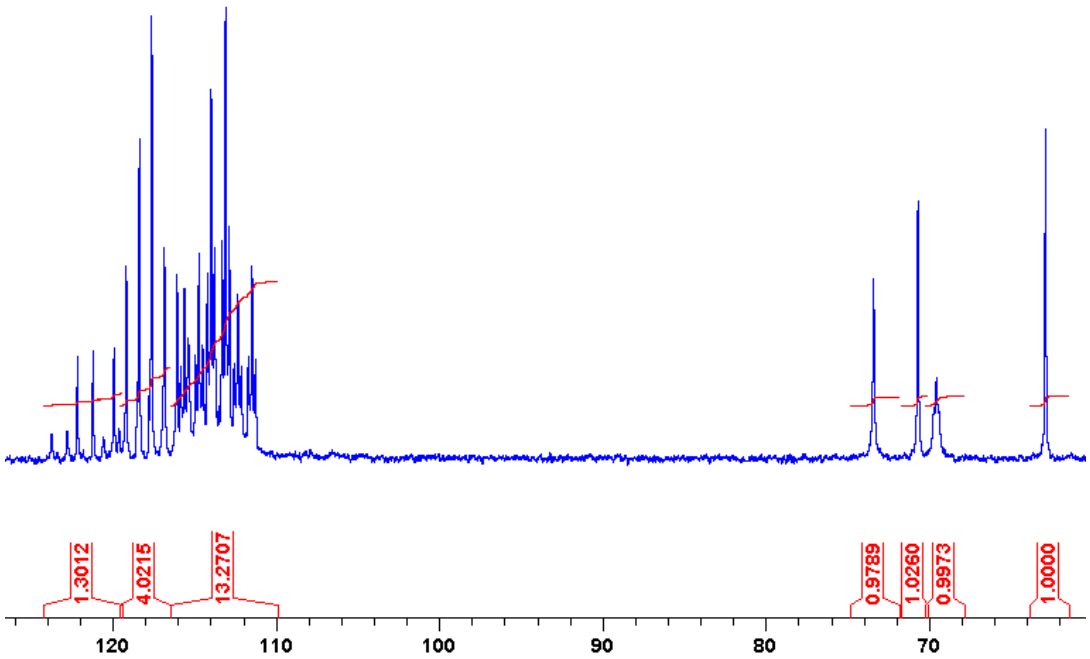


Figure S-26: ^{13}C NMR spectrum of equilibrium neat PFPE tetraol sample. The spectrum is divided

into different regions as indicated for estimation of spin lattice relaxation time.

^{13}C T_1 values of the perfluoro fragments were found to be longer (1.5 o 2.2 sec) compared to that of the end group carbons which were ~an order lower (0.2 to 0.46 sec) for the neat sample. **Table S-4** summarizes the T_1 values of various carbons as a function of hydration. No appreciable changes in the T_1 values are observed within the hydration regimes measured for different carbons except for some of the carbons of the end groups which showed an increasing trend. This probably indicates that local motions of the chains are either not much affected by hydration or the local motions of the molecules are in the T_1 minimum regime, where the variation in T_1 values are insignificant

Table S-4: ^{13}C Spin lattice relaxation times

% Hydration	^{13}C T_1 values (sec)						
	124 to 119 ppm	119 to 116 ppm	116-110 ppm	73.4 ppm	70.7 ppm	69.5 ppm	62.9 ppm
0	1.5	2.2	1.6	0.29	0.46	0.35	0.25
1	1.5	2.2	1.5	0.31	0.49	0.36	0.28
3	1.4	2.2	1.6	0.36	0.57	0.37	0.32
6.5	1.7	2.1	1.5	0.41	0.64	0.37	0.31

^{13}C spin-spin relaxation time (T_2) measurements were performed by using the CPMG pulse sequence where the refocusing time is varied by changing the loop times of the 180 degree pulse. Only the signals of the end group carbons were considered for the T_2 measurements for the fluorinated carbon signals were found to be practically unaffected (**Figures S 23-25**).

Comparison of ^{13}C T_2 plots of neat and hydrated PFPE are shown in Fig S-27 and the T_2 values are given in **Table S-5**. The hydrated samples (3 wt %, 6.5 wt %) showed a better fit with two components whereas a single component fit was sufficient for the neat and 1 wt % samples.

Table S-5: ^{13}C Spin spin relaxation times (T_2)*

% Hydration	^{13}C T_2 values (msec)		
	73.4 ppm	70.7 ppm	62.9 ppm
0	50.3	39.1	64.8
1	43.1	29.5	59.1
3	35.9 (5.0,39.6)	17.0 (10.4,28.8)	43.8 (0.2,43.7)
6.5	16.1 (8.4,20.4)	4.3 (2.4,9.9)	14.7 (7.8,36.2)

*values from 2 component fit

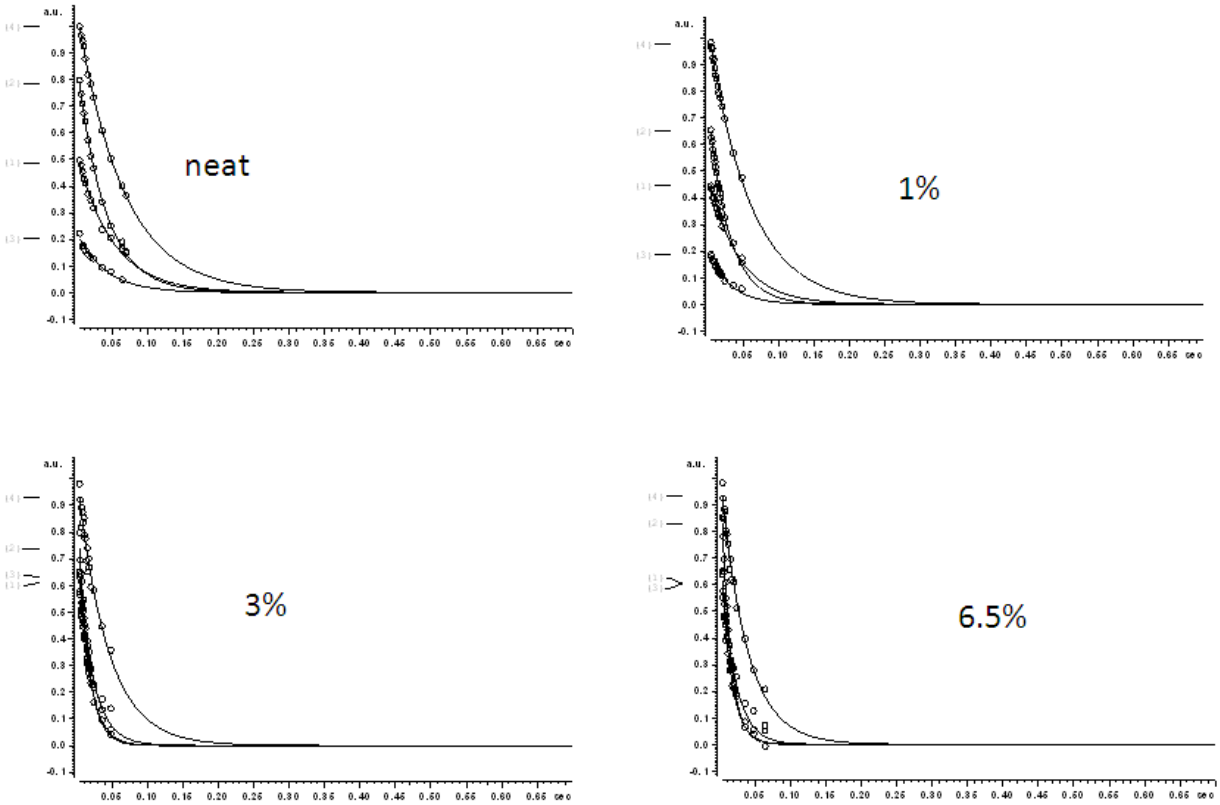


Figure S-27: Comparison of ^{13}C T_2 plots of neat and hydrated PFPE tetraol, hydration levels are indicated. The X axis of plots is kept constant to bring out the decrease in T_2 visually.

It is clear from **Figure S-27** and data in **Table S-5** that ^{13}C signals of the end groups decay faster as the levels of hydration increases. This clearly suggests restrictions in the local motions of these fragments of PFPE due to gelation. This observation taken together with the invariant and/or slight increasing trend of T_1 suggest that the systems under investigation are likely to experience molecular motions with correlation times in the intermediate region 10^{-10} to 10^{-8} sec ($\omega_0\tau_c \approx 1$) where, a T_1 minimum and decrease in T_2 are expected. Further, the system shows a tendency to acquire longer correlation time on hydration as indicated by marginal increase in T_1 of the end group carbons.

It may be stated here that the inference on the correlation time can be confirmed only by a detailed variable temperature T_1, T_2 measurements of these systems which is beyond the scope of the present study.

3. DSC

About 4 to 7 mg of PFPE tetraol gel samples and neat PFPE tetraol were weighed in a tarred hermetic pan and sealed with lid. An empty sealed hermetic pan was used as a reference. Pan containing the specimen was kept in the differential scanning calorimeter (Model Q-10, TA Instruments, USA), equilibrated at 25 °C and kept isothermal for 15 minutes. After equilibration, specimen was cooled from 25 °C to -60 °C at a cooling rate of 1°C / minute. In the second cycle, specimen was heated back to 40 °C at the heating rate of 10 °C / minute. Hermetically sealed saturated PFPE tetraol gels after the calorimetric measurements were stored in vacuum and measured again at regular time intervals.

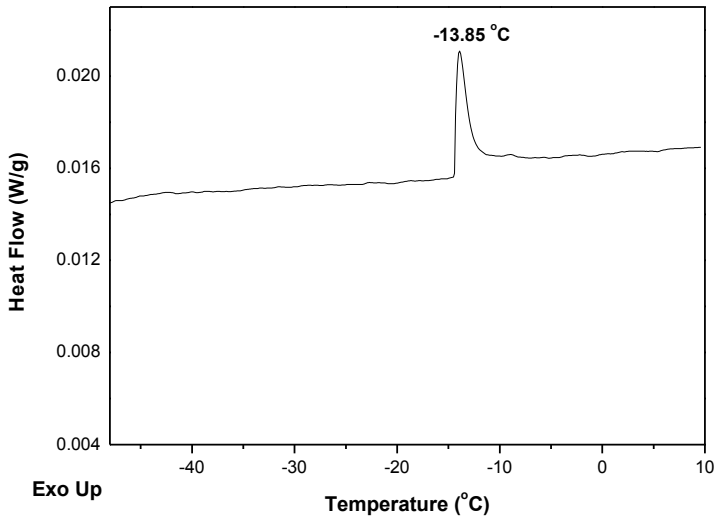


Figure S-28: DSC thermogram of neat de-ionized water

References:

1. Solvay Internal Report, 2012.
2. K. Toukan and A. Rahman, *Phys. Rev. B*, 1985, **31**, 2643-2648.
3. O. Wagner, B. N. S. Thota, B. Schade, F. Neumann, J. L. Cuellar, C. Bottcher and R. Haag, *Polym.Chem.*, 2016, **7**, 2222-2229.