Supporting Information

Effect of solvent quality on the solution properties of assemblies of partially-fluorinated amphiphilic diblock copolymers

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S1.

The ^{1}H NMR spectra of the amphiphilic copolymers in DMF-d_7 are shown in Figure S1. In the spectrum of PAA-*b*-p(*n*BA-*co*-TFEA) (Figure 1(A)), the peaks marked from *a* to *l* could be assigned to the characteristic signals of protons of the PAA, P*n*BA and PTFEA segments. The peaks labelled *b* (2.55 ppm), *h* (2.46 ppm) and *e* (2.58 ppm) are assigned to the methine protons (–$CH_2C\mathbf{H}$(CO)–)) in the backbone belonging to PAA, P*n*BA and PTFEA. The peaks *f* at 4.76 ppm and *i* at 4.06 ppm were assigned to the methylene protons (–$C\mathbf{H}_2$CH(CO)–)) attached to the ester bond in the side chain belonging to PTFEA and P*n*BA blocks, and peak *c* at 12.6 ppm was assigned to the carboxylic acid protons of PAA. The ^{1}H NMR spectra of PAA-*b*-p(*n*BA-*co*-TFEMA) were similar to PAA-*b*-p(*n*BA-*co*-TFEA) (see for example Figure 1(B)), but there are only two methine protons (–$CH_2C\mathbf{H}$(CO)–), peak *b* at 2.55 ppm, and *h* at 2.45 ppm belonging to PAA and P*n*BA and a new resonance arising from the methyl protons (–$C\mathbf{H}_3$), *e*, 0.93 ppm) due to TFEMA.

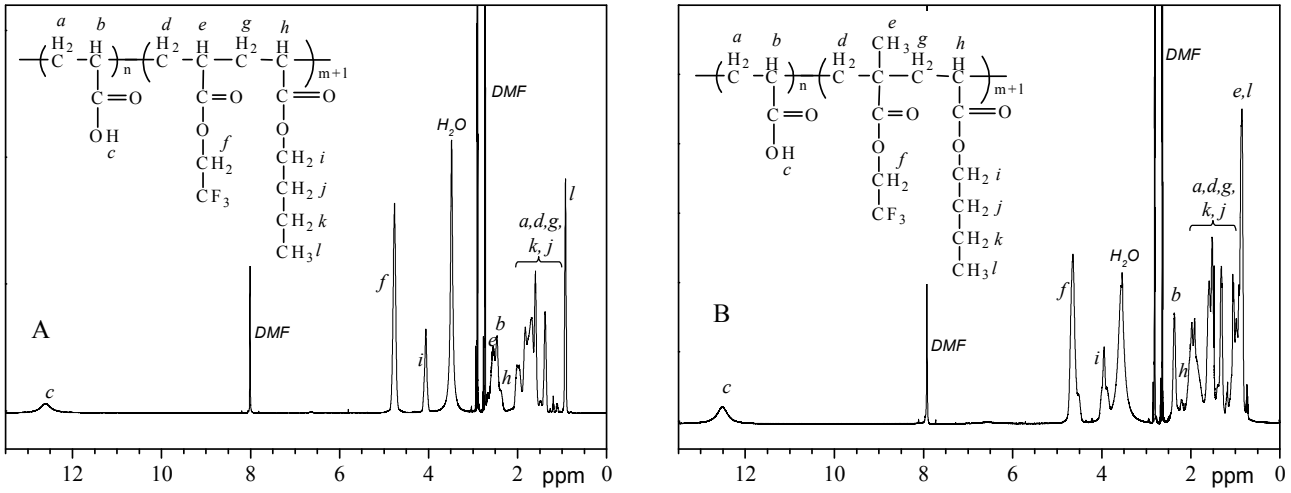


Figure S1. The ^{1}H NMR spectra of (A) PAA_{50}-*b*-P(*n*BA_{39}-*co*-$TFEA_{115}$) and (B) PAA_{52}-*b*-P(*n*BA_{39}-*co*-$TFEMA_{103}$) in DMF-d_7.

S2.

The Flory-Huggins interaction parameter between blocks $\chi_{A\text{-}B}$ can be estimated by [1]

$$\chi_{A-B} = \frac{V_r(\delta_A - \delta_B)^2}{RT}$$

where V_r is the molar volume of the blocks, R is the gas constant, T is the temperature (298 k), and δ_A and δ_B are the solubility parameters of the different blocks, respectively. [2]

	PAA	P*n*BA	PTFEA	PTFEMA
Solubility parameters (δ_A) ($MPa^{1/2}$)	24.6			
Solubility parameters (δ_B) ($MPa^{1/2}$)		18.0	17.5	17.1
Molar volume (V_r) $(cm^3/mol^{-1})^2$	58.76	122.54	102.01	118.29

1. Polymer Handbook, 4th ed.; Brandrup, J.; Immergut,E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R., Eds. Wiley: New York, 1999.P521
2. D.W. Van Krevelen, Properties of polymers : their correlation with chemical structure; their numerical estimation and prediction from additive group contributions , Elsevier (Amsterdam), 1990.

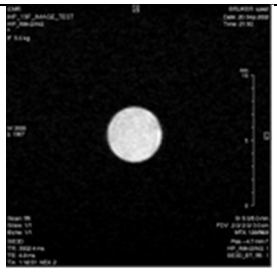
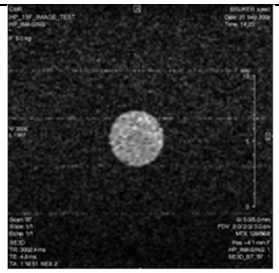
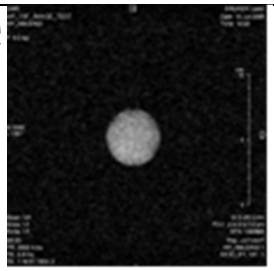
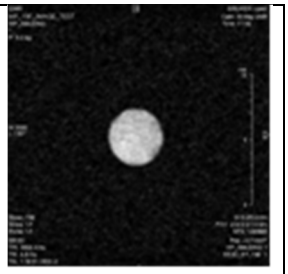
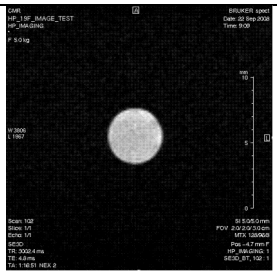
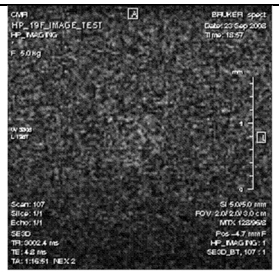
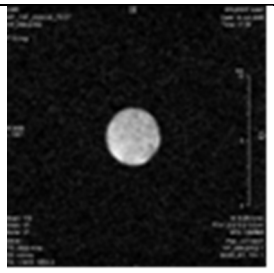
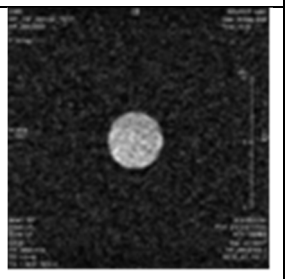
A 	B 	C 	D 
DMF S/N=41.0	DMF:D_2O=1:1 S/N=8.8	Acetone S/N=20.7	Acetone:D_2O=1:1 S/N=17.5
PAA_{50}-*b*-P(*n*BA_{39}-*co*-$TFEA_{115}$) 2.0 wt.%; RT (S/N: Signal-to-Noise Ratio)			
E 	F 	G 	H 
DMF S/N=27.8	DMF:D_2O=1:1 S/N=2.4	Acetone S/N=17.8	Acetone:D_2O=1:1 S/N=8.9
PAA_{52}-*b*-P(*n*BA_{39}-*co*-$TFEMA_{103}$) 2.0 wt.%; RT (S/N: Signal-to-Noise Ratio)			

Figure S3. Selected slices from the 3D spin echo ^{19}F MRI images of solutions of block copolymer assemblies in mixed solvent. The field of view in each case is 20×20 mm^2.