Soft Matter

ARTICLE

Gelation of Fmoc-diphenylalanine is a first order phase transition

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

SUPPLEMENTARY INFORMATION

Nikola A. Dudukovic*[a] and Charles F. Zukoski[b]

^{1}H DOSY (PFGSE) NMR measurements

Pulsed field gradient spin echo nuclear magnetic resonance (PFGSE NMR) utilizes the attenuation of the echo signal from a spin-echo pulse sequence containing a magnetic field gradient pulse at each period to determine the displacement of the observed spins on timescales of milliseconds to seconds.[37,38] The position of a spin an ensemble of diffusing nuclei in the *z*-direction can be "labeled" by applying a well-defined magnetic field gradient. When a 90º gradient pulse (δ) is applied at time t_1, the spin experiences a phase shift, which has two terms: (1) phase shift due to the main field B_0 and (2) phase shift due to the gradient g. Applying the following 180º pulse after period τ reverses the precession sign. When the 90º echo is applied at time t_1+Δ the spin experiences the same main field phase shift, but the phase shift due to the gradient will differ if the molecule has moved from position $z(t_1)$ to $z(t_2)$. The total phase shift at the end of the pulse echo sequence is given by:[37]

$$\varphi_i(2\tau)=\left\{\gamma B_0\tau+\gamma g\int_{t_1}^{t_1+\delta} z_i(t)dt\right\}-\left\{\gamma B_0\tau+\gamma g\int_{t_1+\Delta}^{t_1+\Delta+\delta} z_i(t')dt'\right\} \quad \text{(S1)}$$

where $\gamma = \omega_0/B_0$ is the gyromagnetic ratio of the Larmor frequency and strength of the static magnetic field.

Diffusion of the spins D_S can be correlated to the attenuation of a spin echo signal $S(t)$ resulting from the dephasing of the nuclear spins due to the combination of the translational motion of the spins and the imposition of the spatially defined gradient pulses:[37,38]

$$\frac{dS(t)}{dt}=-\gamma^2 D_S\left[\int_0^t g(t')dt'-2H(t-\tau)\int_0^\tau g(t')dt'\right]^2 S(t) \quad \text{(S2)}$$

By integrating Eq. (S2) from 0 to 2τ the following relationship is obtained:

$$\ln\left[\frac{S(2\tau)}{S(0)}\right]=-\gamma^2 g^2 D_S\delta^2(\Delta-\delta/3) \quad \text{(S3)}$$

Full ^{1}H NMR spectrum of Fmoc-FF in DMSO

The full ^{1}H NMR spectrum of Fmoc-FF dissolved in deuterated DMSO at volume fraction of $\phi_{Fmoc\text{-}FF} = 0.052$ is given in **Figure S1**.

Expressions used in calculations of D_2

Calculation of mobility functions A_{11} and A_{12} (Jeffrey and Onishi)[34]

$$A_{11}=\sum_{k=0}^{\infty} f_{2k}(\lambda)(1+\lambda)^{-2k}s^{-2k} \quad \text{(S4)}$$

$$A_{12}=-\frac{1}{2}(1+\lambda)\sum_{k=0}^{\infty} f_{2k+1}(\lambda)(1+\lambda)^{-2k-1}s^{2k-1} \quad \text{(S5)}$$

where:

$$s=\frac{2r}{a_1+a_2} \quad \text{(S6)}$$

$$\lambda=\frac{a_2}{a_1} \quad \text{(S7)}$$

For $0 \le k \le 11$, functions f_{2k} and f_{2k+1} are calculated as:

[a] Address here.
[b] Address here.
[c] Address here.
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

$f_0 = 1$
$f_1 = -3$
$f_2 = 0$
$f_3 = 4 + 4\lambda^2$
$f_4 = -60\lambda^3$
$f_5 = 0$
$f_6 = 480\lambda^3 - 128\lambda^5$
$f_7 = -2400\lambda^3$
$f_8 = -960\lambda^3 + 4224\lambda^5 - 576\lambda^7$
$f_9 = 1920\lambda^3 + 1920\lambda^5$
$f_{10} = -17920\lambda^5 - 96000\lambda^6 + 30720\lambda^7 - 2304\lambda^9$
$f_{11} = -15360\lambda^3 + 231936\lambda^5 - 15360\lambda^7$

Calculation of mobility functions B_{11} and B_{12} (Jeffrey and Onishi)[34]

$$B_{11} = \sum_{k=0}^{\infty} f_{2k}(\lambda)(1+\lambda)^{-2k} s^{-2k} \tag{S8}$$

$$B_{12} = \frac{1}{2}(1+\lambda)\sum_{k=0}^{\infty} f_{2k+1}(\lambda)(1+\lambda)^{-2k-1} s^{-2k-1} \tag{S9}$$

For $0 \le k \le 11$, functions f_{2k} and f_{2k+1} are calculated as:

$f_0 = 1$
$f_1 = 3/2$
$f_2 = 0$
$f_3 = 2 + 2\lambda^2$
$f_4 = 0$
$f_5 = 0$
$f_6 = -68\lambda^5$
$f_7 = 0$
$f_8 = -320\lambda^3 + 288\lambda^5 - 288\lambda^7$
$f_9 = 0$
$f_{10} = -6720\lambda^5 - 3456\lambda^7 - 1152\lambda^9$
$f_{11} = 8960\lambda^3 + 8848\lambda^5 - 8960\lambda^7$

Perturbation of the pair distribution function Q for $\lambda = 2$ (Batchelor)[33]

The numerical solution for Q by Batchelor is given in **Figure S2**.

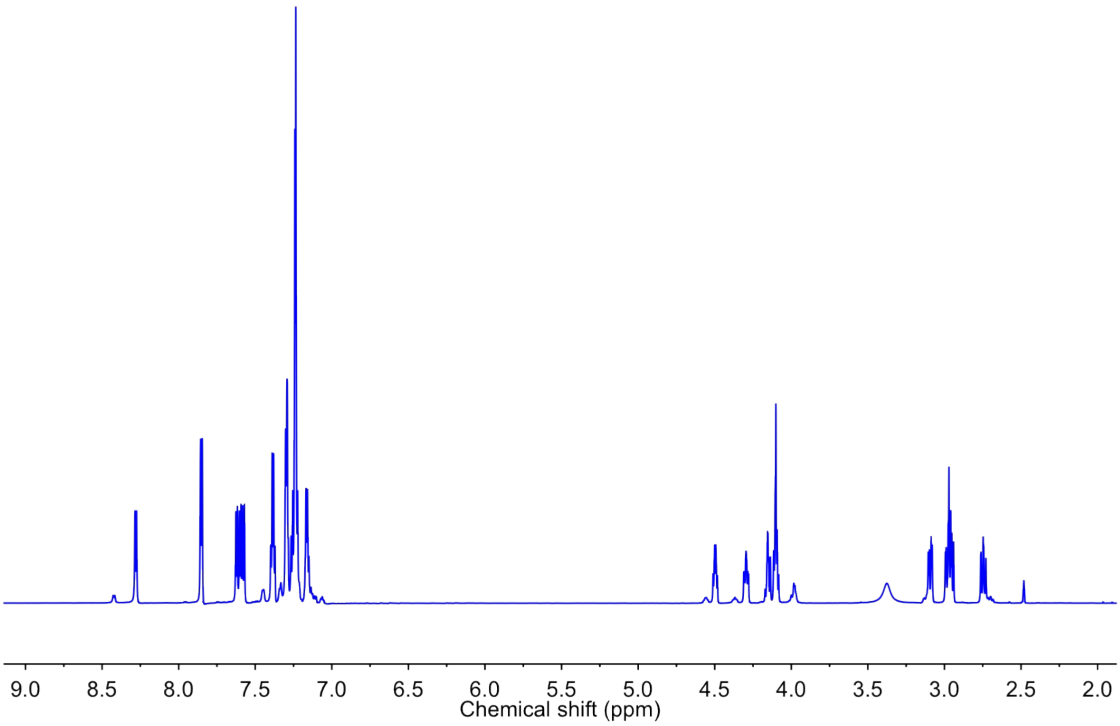

Figure S1. ^{1}H NMR spectrum of Fmoc-FF in deuterated DMSO.

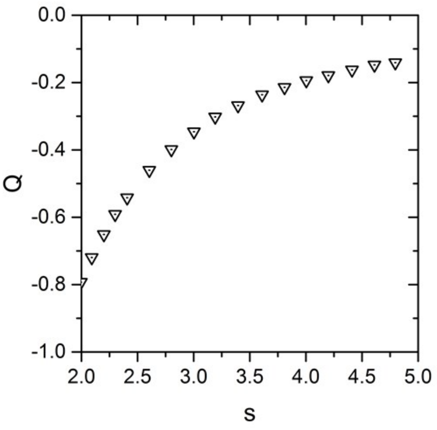

Figure S2. Numerical solution for pair distribution function Q (λ = 2).[33]

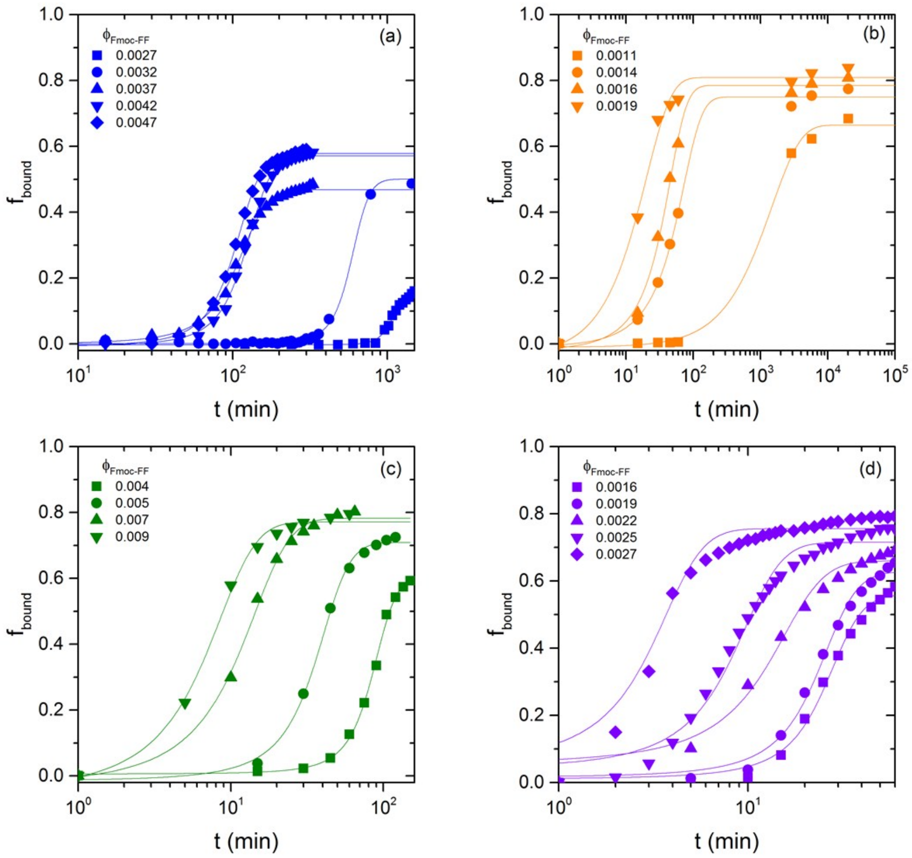

Figure S3. Fraction of Fmoc-FF molecules bound in the solid phase at various Fmoc-FF volume fractions and water concentrations x_{H2O} of: (a) 0.25; (b) 0.30; (c) 0.35; (d) 0.40.

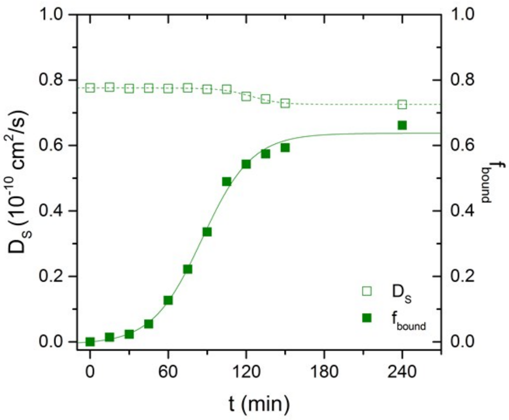

Figure S4. Self-diffusivity D_S of freely diffusing Fmoc-FF molecules in a slowly gelling sample ($\phi_{Fmoc\text{-}FF}$ = 0.004, x_{H2O} = 0.35) and corresponding fraction of bound molecules f_{bound}.