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<p style="text-align:center">Supporting Information</p>

NMR Study of the Dissolution of Core-Crystalline Micelles

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ADDITIONAL RESULTS AND DISCUSSION

Viscosity of decane at different temperatures

In order to convert diffusion coefficients determined at different temperatures to hydrodynamic radii, we needed values of the viscosity of decane at these temperatures. These viscosity values are known for some temperatures, but in order to interpolate values over the entire range, we measured D_s values of neat decane over the entire temperature range. [1] At 25 °C, where the viscosity of decane is known, we calculated $R_h = 0.19$ nm from the measured D_s value and the Stokes-Einstein expression.[2] Since decane is a small organic molecule, we assumed that the magnitude of R_h would not change significantly in this temperature range. Values of the measured D_s and corresponding calculated solvent viscosity values, η, are collected in Table S1. In Figure S2 the experimental viscosities are compared with the reported literature values[3] and show a good match.

Further analysis of DOSY NMR decays showing two components

As described in the main text, the decay of the DOSY NMR signal for the PI protons in micelle fragments of PFS$_{65}$-b-PI$_{637}$ at 70, 75, 80, and 85 °C were fitted to a sum of two exponential terms, yielding diffusion coefficients for fast diffusing unimer and the slower diffusing surviving micelle fragments. According to eqs 5 and 6 in the main text, reproduced here, the fraction of polymer associated with the fast decay (f_{uni}) and slow decay (f_{mic}) can be calculated if the T_1 and T_2 relaxation times of both species at each temperature were known.

$$A_{uni}/A_{mic} = [f_{uni}\exp(-2\tau_2/T_{2uni})\exp(-\tau_1/T_{1uni})] / [f_{mic}\exp(-2\tau_2/T_{2mic})\exp(-\tau_1/T_{1mic})] \tag{5}$$

$$f_{uni} + f_{mic} = 1 \tag{6}$$

where A_{uni} and A_{mic} are the pre-exponential factors obtained from fitting the measured DOSY NMR decays to a sum of two exponential terms. In all measurements, τ_2 was set to 5 ms and τ_1 varied with the diffusion delay time following the expression $\Delta = \tau_2 + \tau_1$.

Since it is not possible to obtain measure separate values of T_1 and T_2 when both species are present and have resonances at the same chemical shift, further assumptions about the data are necessary. To proceed, we make the strong assumption that values of T_1 and T_2 for the unimer can be taken from the measured values for the PFS$_{65}$-b-PI$_{637}$ molecules dissolved in benzene-d6 ($T_1 = 0.68$ s; $T_2 = 0.24$ s). We also assume that corresponding values of the micelle fragments can be taken from the measured values for the micelle fragments ($T_1 = 0.65$ s; $T_2 = $

0.069 s) in decane at 25 °C. The weakness of these assumptions is that these relaxation times likely depend upon solvent and temperature.

By making these assumptions, we calculate apparent compositions of the solutions at 70, 75, 80, and 85 °C. These compositions, collected in Table S2, are close to values determined by VT NMR for the three highest temperatures. For 70 °C, the unimer contribution to the overall signal is small. While the fit to the DOSY NMR decays gives reasonable values of R_h, the fraction f_{uni} is overestimated. At 90 and 95 °C, small amounts of surviving micelle fragments can be inferred from the VT NMR peak integrations, but their contribution to the DOSY NMR decays is too small to be detected.

Analysis of the NMR signals of PI block at high temperatures

Decane is a good solvent for the PI block at both room temperature and high temperatures. An internal standard, ferrocene, was used to test the changes in PI integration with temperature and the resulting NMR spectra taken at 25 °C and 100 °C are shown in Figure S8. The ferrocene peak is a singlet located at 4.05 ppm and its integration was normalized to 1 in both spectra. The integrations of the PI block were 1.82 at 25 °C and 1.84 at 100 °C, and this intensity difference is negligible.
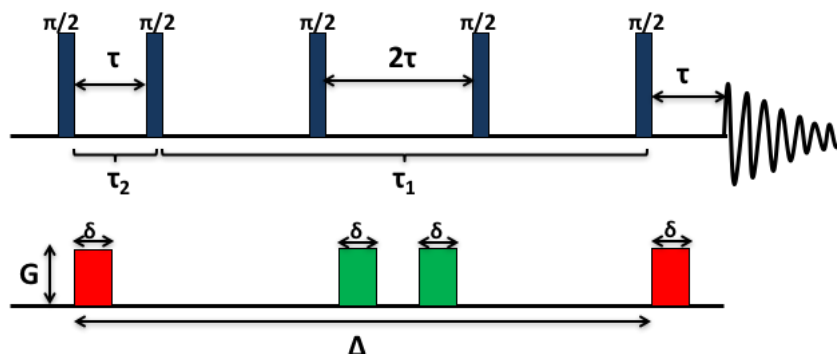
ADDITIONAL FIGURES

Figure S1. The stimulated-echo pulsed field gradient NMR (PFG NMR) sequence with convection compensation. A 90 ° pulse is introduced halfway through the diffusion delay to move the magnetization to the transverse plane, followed by a gradient pulse (green) to refocus. A second gradient pulse (green) that is identical to the first one will phase label the spins in the opposite direction, and then a 90 ° pulse will convert the magnetization back to axial for the second half of the diffusion delay. As the convection in the sample tube is in an ordered system and the convection velocity is constant during the diffusion delay, the phase evolution due to convection is opposite during the two halves of the diffusion delay and compensate each other[4-5]. Therefore, the introduction of two 90 ° pulse and two gradient pulses in the middle of diffusion can help us eliminate convection issues in elevated temperatures.
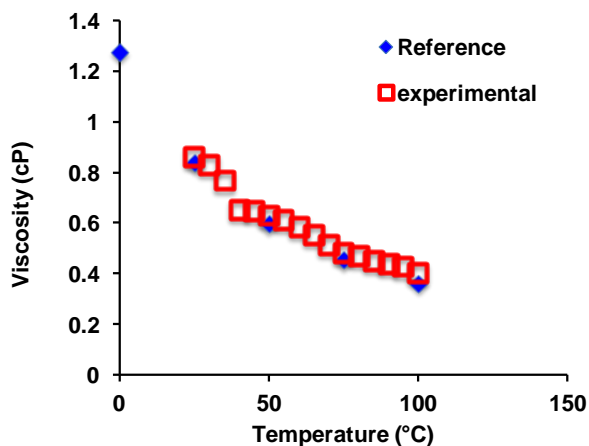

Figure S2. Comparison of experimental and literature values of the viscosities of decane at various temperatures from 0 to 100 °C.[3]
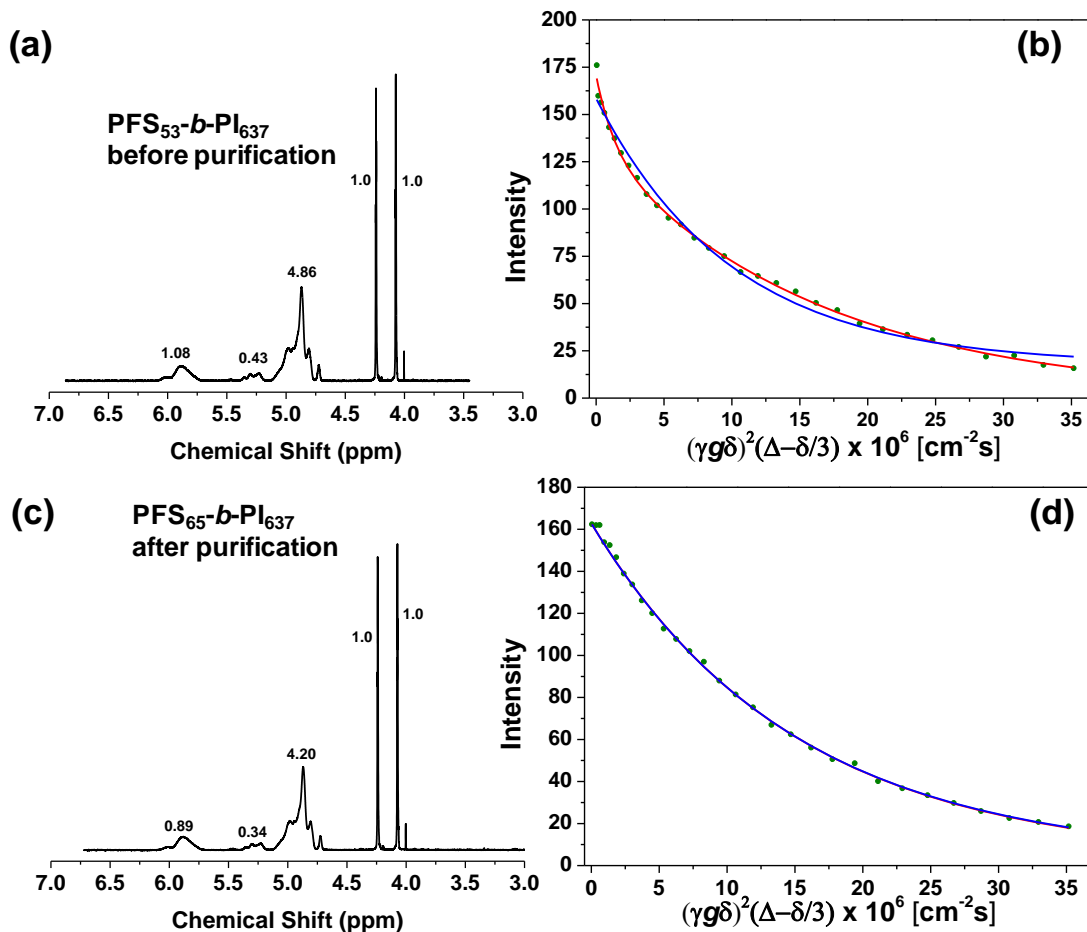
Figure S3. ^{1}H NMR spectra of the original "PFS$_{53}$-*b*-PI$_{637}$" sample in C$_6$D$_6$ **(a)** before and **(c)** after purification to remove a small amount of PI$_{637}$ homopolymer impurity. The calculated composition changed to PFS$_{65}$-*b*-PI$_{637}$ after purification by fractional precipitation. Stimulated echo intensity attenuation Intensities of the NMR signal at 4.4-5.1 ppm as a function of the gradient strength at 25 °C. The NMR signal is due to resonances of PI protons from micelle fragment samples in decane prepared from **(b)** "PFS$_{53}$-*b*-PI$_{637}$" prior to purification and **(d)** from PFS$_{65}$-*b*-PI$_{637}$ after purification to remove a PI$_{637}$ homopolymer impurity. The spectra were run with DMSO-d_6 in a capillary insert. In (**b**), the red solid line is the curve of the fit obtained using a two-exponential function, and the blue solid line is the curve of the best fit obtained using a mono-exponential function.
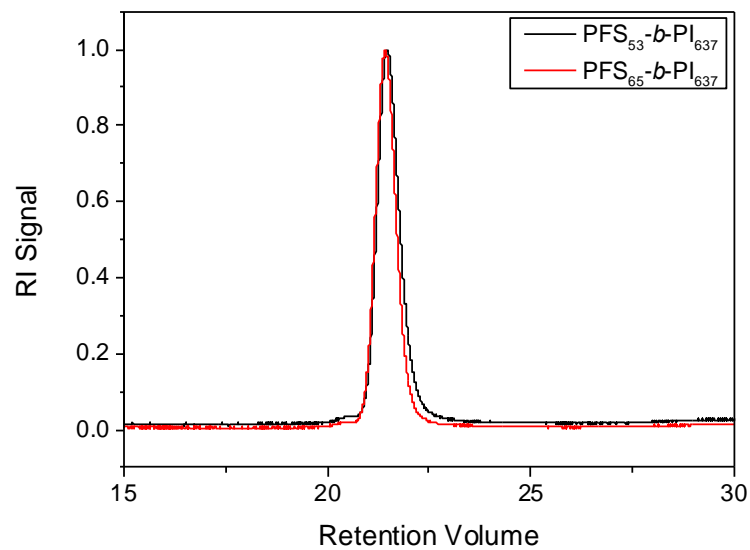
Figure S4. The RI GPC traces of the "PFS$_{53}$-*b*-PI$_{637}$" sample and PFS$_{65}$-*b*-PI$_{637}$ in THF. Both peaks are monomodal and a decrease in Đ from 1.07 to 1.04 was found after purification.
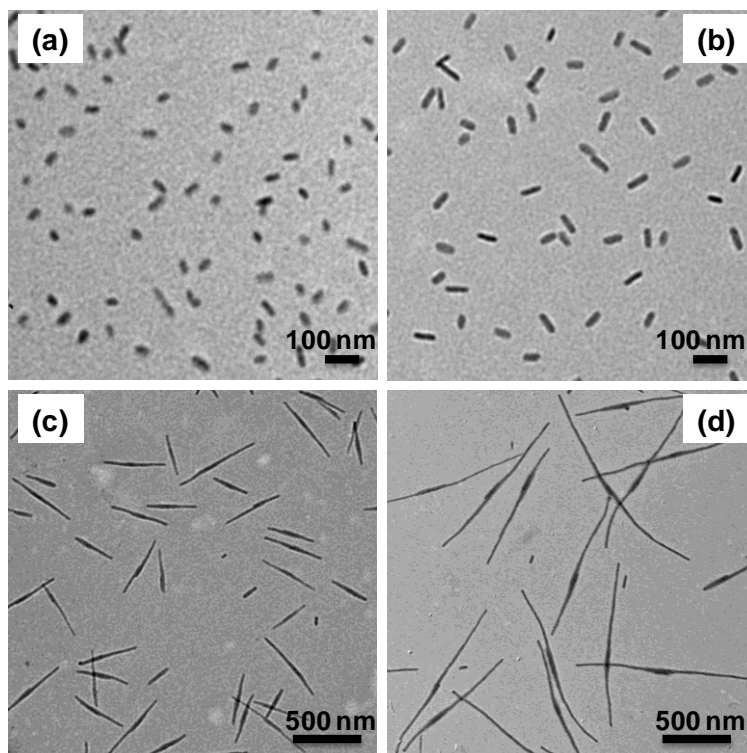

Figure S5. TEM images of the micelle fragments formed upon cooling after DOSY experiments at various temperatures (a) 70, (b) 80, (c) 90, and (d) 100 ºC.
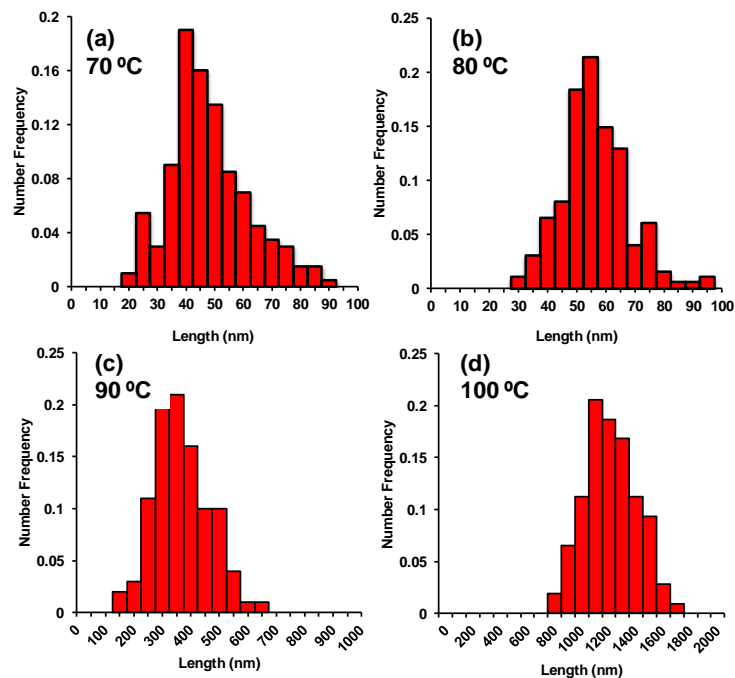
Figure S6. Length distributions of the micelle fragments formed upon cooling after DOSY experiments at various temperatures at **(a)** 70 °C (L_n = 48 nm, L_w/L_n = 1.14), **(b)** 80 °C (L_n = 54 nm, L_w/L_n = 1.04), **(c)** 90 °C (L_n = 392 nm, L_w/L_n = 1.06), and **(d)** 100 °C (L_n = 1264 nm, L_w/L_n = 1.02).
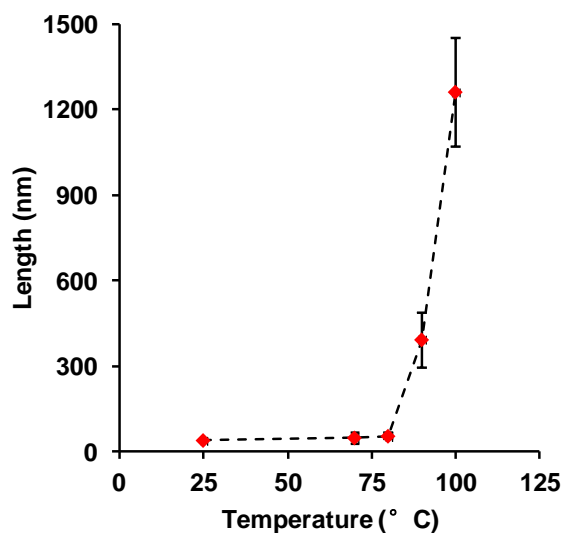

Figure S7. Average micelle length of micelle fragments formed upon cooling after DOSY experiments at various temperatures from 25 to 100 °C.
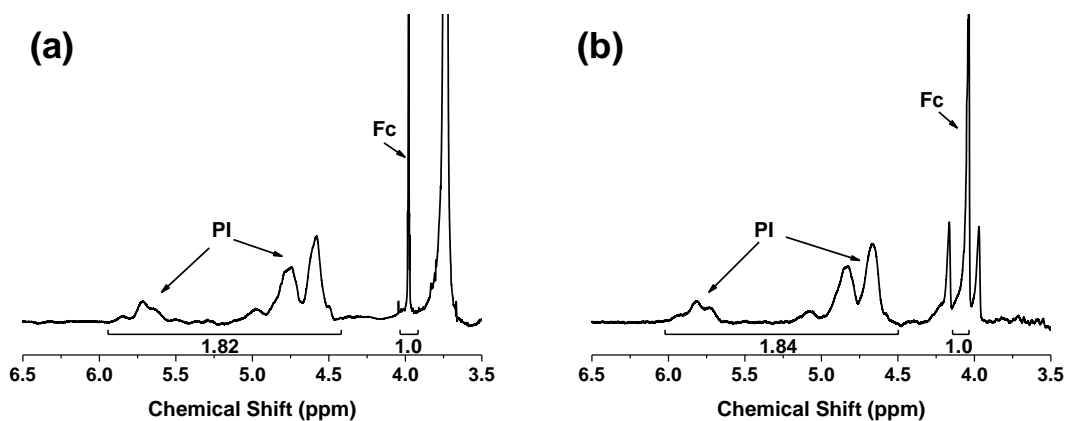
Figure S8. NMR spectra of PFS$_{65}$-*b*-PI$_{637}$ micelles in decane with ferrocene as an internal standard at (a) 25 °C and (b) 100 °C. Ferrocene appears as a singlet at 4.05 ppm.

ADDITIONAL TABLES

Table S1. Template for DOSY experiments of solvent decane [a] with DMSO-*d$_6$*-insert

NMR [b]	Dpfgdste							
Temperature (°C)	25	70	75	80	85	90	95	100
Lowest Gradient	1000	1000	1000	1000	1000	1000	1000	1000
Highest Gradient	4500	4000	3300	3100	3000	2900	2800	2700

a. All experiments were run with a capillary insert containing DMSO-*d$_6$* as deuterium lock.

b. Using relaxation time 5 s, number of scans 4, diffusion gradient length 4.5 ms, diffusion delay 200 ms, grad stab delay 0.5, and 15 increments.

Table S2. Template for DOSY experiments of PFS$_{65}$-b-PI$_{637}$ micelle fragments in decane [a]

Pulse Sequence [b]	Dpfgdste							
Temperature (℃)	25	70	75	80	85	90	95	100
Diffusion delay $\varDelta$ (ms)	900	650	450	200	250	200	150	50

a. All experiments were run with a capillary insert containing DMSO-d_6 as deuterium lock.

b. Using relaxation time 5 s, number of scans 32, gradient range 1000 – 28000, diffusion gradient length 4.5 ms, grad stab delay 0.5, and 31 increments.

Table S3. Experimental diffusion coefficients D_s and viscosities of decane η at various temperatures.

T (K)	$10^5 D_s$ (cm^2/s)	η (cP)	T (K)	$10^5 D_s$ (cm^2/s)	η (cP)
298	1.3	0.86	338	2.4	0.55
303	1.4	0.83	343	2.6	0.51
308	1.6	0.77	348	2.8	0.48
313	1.9	0.65	353	3.0	0.47
318	1.9	0.65	358	3.1	0.45
323	2.0	0.63	363	3.2	0.44
328	2.1	0.61	368	3.3	0.43
333	2.2	0.58	373	3.6	0.40

Table S4. Apparent percent of PFS_{65}-b-PI_{637} present as unimer in decane at various temperatures as inferred from VT- and DOSY NMR

Temperature ℃	% unimer in solution			
	DOSY.01	VT. 01 ^{1}H NMR	DOSY.02	VT.02 ^{1}H NMR
25	0	0	0	0
50	0	0	0	0
70	20	6.1	17	10
75	21	7.7	24	19
80	34	18	28	31
85	51	35	62	55
90	100[a]	48	100[a]	78
95	100[a]	81	100[a]	92
100	100[a]	82	100[a]	99

a. These values are calculated assuming that T_1 and T_2 values for the micelles and unimer unchanged from their values at 25 °C. this assumption is unlikely to be correct. The individual T_1 and T_2 values at elevated temperatures could not be determined.

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