

Supportive Information

Synthesis and self-assembly behavior of poly(N_{α} - Boc-L-tryptophan)-*block*-poly(ethylene glycol)- *block*-poly(N_{α} -Boc-L-tryptophan)

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1. Synthesis

The first 18 samples were synthesised using 1,4-dioxane/ CHCl_3 (3 to 2 ratio) as solvent. DMF was used for sample 19. Feed ratios of starting materials along with concentration of materials in solution, temperature and time allowed for synthesis were all found to be contributing factors to the chain extension achieved. The solvent used for synthesis also seemed to carry an overbearing effect over chain extension with higher molecular weight hydrophobic blocks being achieved in DMF compared to 1,4-dioxane/ CHCl_3 , when using the same starting material ratio and concentration in solution, the same reaction temperature, whilst allowing less reaction time. The drawback of using DMF as a solvent was its high boiling point making it harder to remove *in vacuo*, with its complete removal only being achieved following subsequent dialysis into water.

The influence of concentrations in solution, reaction time allowed, temperature and solvent used are reported in Table 1S below.

Table 1S. Library of 19 copolymers displaying the effects of feed ratios, concentration, temperature and time on BocLTrp monomer attachment, M_n and yield of PBocLTrp-*b*-PEG-*b*-PBocLTrp copolymers.

BAB Number	BAPEG : BocLTrp Feed	Conc (w/v %) (g/ml)	Temp (°C)	Time (hrs)	M_n^{**}	BocLTrp attached	Yield %
1*	2 : 1	5	40	72	5,002	5	69
2	1 : 1	5	40	72	4,672	4	53
3	1 : 1.3	5	40	120	5,332	9	58
4	1 : 1	5	40	72	6,654	10	44
5	1 : 2	3	40	72	3,350	0	0
6	1 : 1.8	3	50	72	3,350	0	0
7	1 : 1.8	5	40	72	7,976	14	49
8*	1 : 1.8	5	40	120	11,940	26	59
9	1 : 1.8	5	50	72	6,654	10	55
10*	1 : 2	5	40	72	13,923	32	66
11	1 : 2.5	3	40	96	3,350	0	0
12	1 : 2.5	3	50	96	5,993	8	38
13	1 : 2.5	5	40	96	7,976	14	46
14	1 : 3	5	40	72	4,011	4	24
15	1 : 3.5	3	40	96	7,976	14	28
16	1 : 3.5	5	40	72	3,350	0	0
17	1 : 5	5	40	72	13,592	31	27
18	1 : 11	5	40	72	11,610	25	78
19*	1 : 1.8	5	40	96	16,566	40	80

* copolymers selected for further self-assembly studies ** as calculated through ^1H NMR integrations.

2. 2D-NMR

2D NMR spectra were measured on a Jeol Eclipse JNM-EX400 MHz spectrometer as. All spectra were collected at room temperature using the residual proton resonance of the CDCl₃ as the internal standard. Proton signals reported as chemical shift σ (ppm).

Heteronuclear Multiple-Bond Correlation (HMBC), a proton detected 2D experiment providing information about direct through bond proton carbon interactions, was used. The x frequency axis represents the ¹H spectrum of the molecule of interest whilst the y axis represents its ¹³C spectrum.

Another proton detected experiment employed was the Heteronuclear Multiple-Bond Correlation (HMBC). This method will generally detect $^2J_{CH}$ and $^3J_{CH}$, with $^4J_{CH}$ sometimes observed. Not all long-range coupling will be observed, therefore HMBC experiments need to be supported by other 2D data for comprehensive structure elucidation. The x and y frequency axes are plotted in the same manner as for a HMQC experiment.

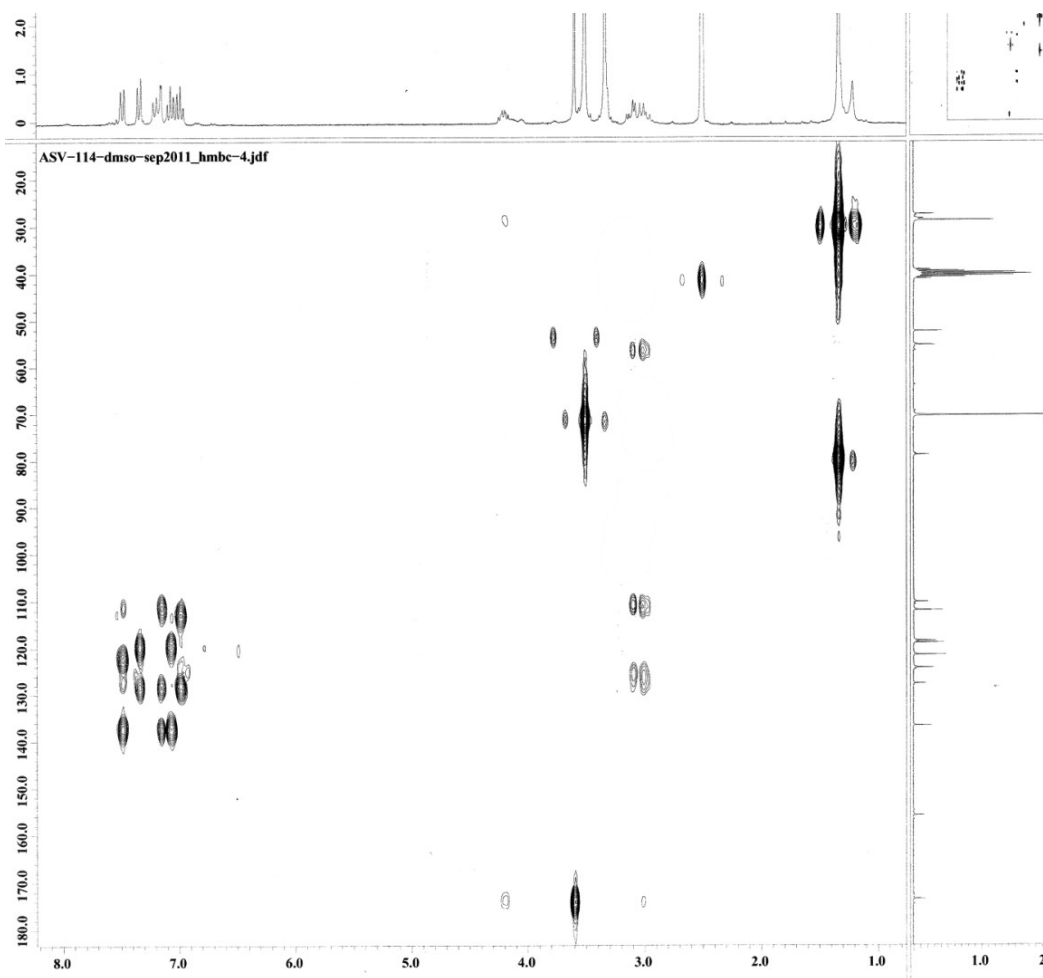


Figure 1S. HMBC spectrum of PBocLTrp-*b*-PEG-*b*-PBocLTrp copolymer in d_6 -DMSO.

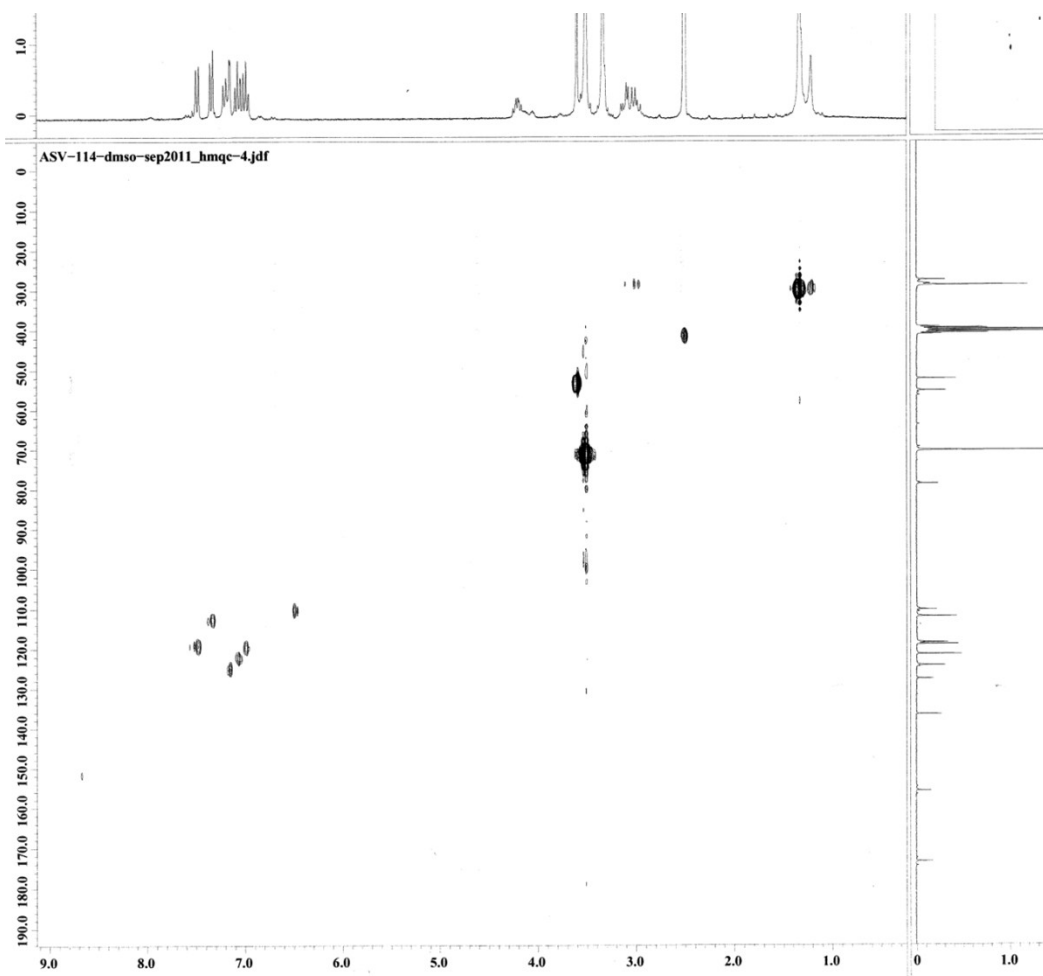


Figure 2S. HMQC spectrum of PBocLTrp-*b*-PEG-*b*-PBocLTrp copolymer in d_6 -DMSO.

Table 2S. HMBC correlations for PBocLTrp-*b*-PEG-*b*-PBocLTrp in *d*₆-DMSO.

¹ H δ (ppm)	¹³ C δ (ppm)
10.85	110.3 127.62 136.67
7.53	110.3 121.5 127.62 136.67
7.34	118.96 127.62
7.12-7.26	110.3 127.62 136.67
7.07	118.55 136.67
6.99	112.01 127.62
4.13	27.39 173.51
3.05	127.62 173.51

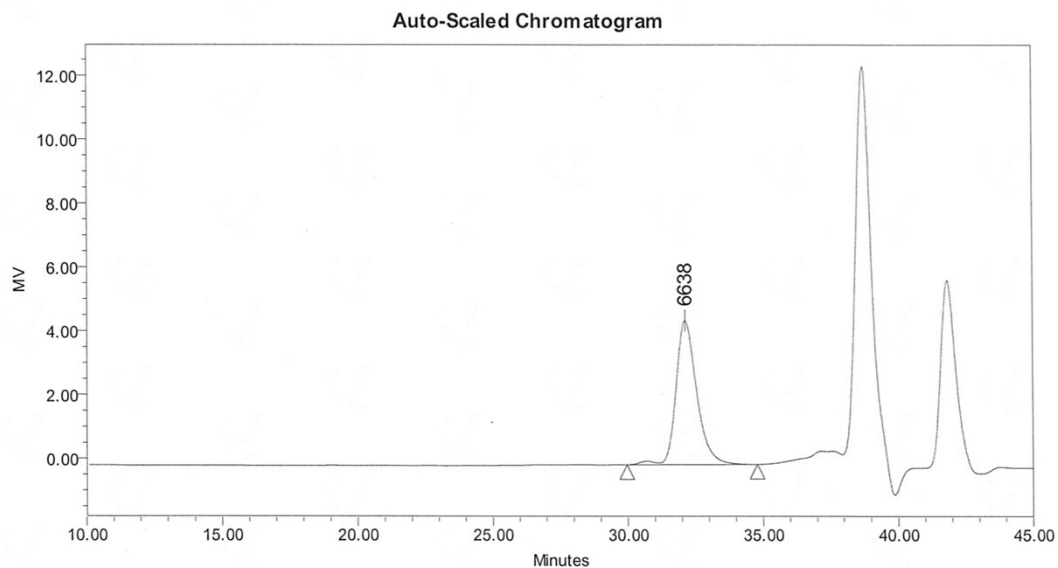
Table 3S. Complete structure assignment of PBocLTrp-*b*-PEG-*b*-PBocLTrp copolymers in d_6 -DMSO.

^{13}C δ (ppm)	DEPT-135 elucidation	^1H attached (ppm)*	^1H multiplicity	Molecule assignment**
173.51	Quaternary	-----	-----	t-Boc C=O
155.94	Quaternary	-----	-----	C=O
136.67	Quaternary	-----	-----	C-NH
127.62	Quaternary	-----	-----	Indole quaternary
124.3	CH	7.12-7.26	m	C2
121.5	CH	7.07	t	C5
118.96	CH	6.99	t	C6
118.55	CH	7.53	d	C4
112.01	CH	7.34	d	C7
110.3	Quaternary	-----	-----	C3
78.81	Quaternary	-----	-----	t-Boc
70.36	CH ₂	3.51	s	PEG CH ₂
55.25	CH	4.13	m	α -C
27.39	CH ₂	3.05	m	β -C
28.70	CH ₃	1.33	s	t-Boc CH ₃

(*As determined from HMQC experiments. **As determined from HMBC, HMQC and DEPT-135).

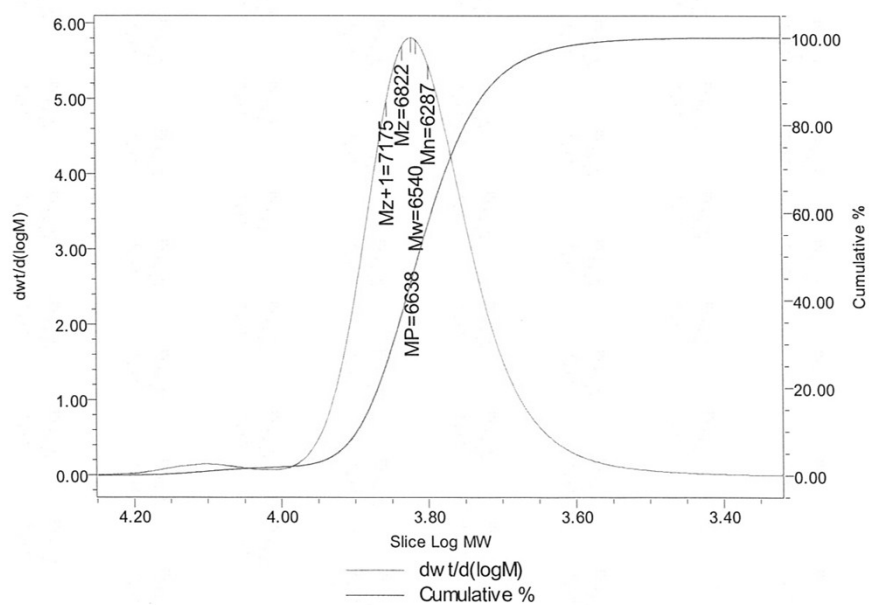
3. GPC

BAB 5000



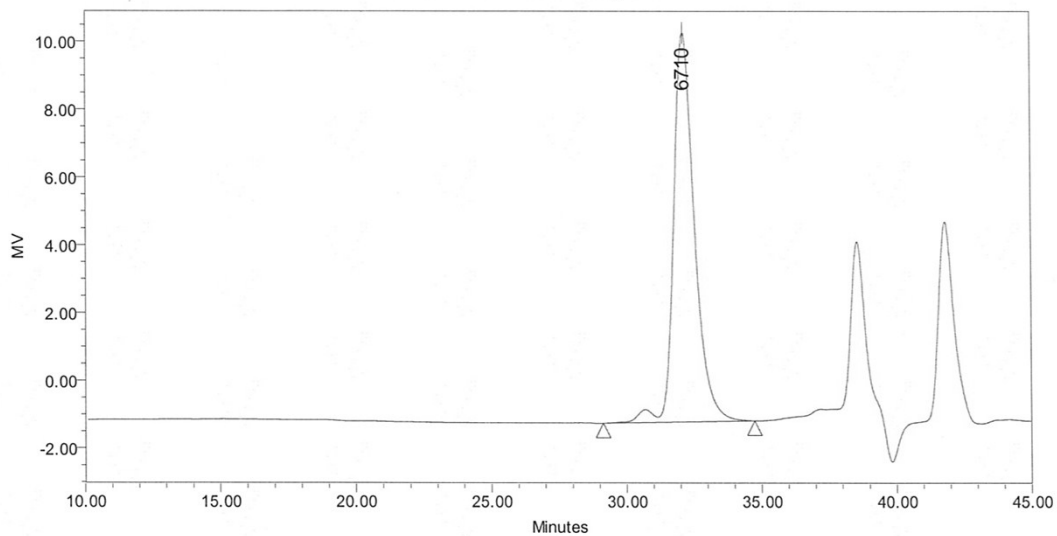
GPC Results

	Retention Time	Adjusted RT	Mn	Mw	MP	Mz	Mz+1	Poly dispersity	Baseline Start	Baseline End
1	32.130	32.130	6287	6540	6638	6822	7175	1.040142	29.967	34.800



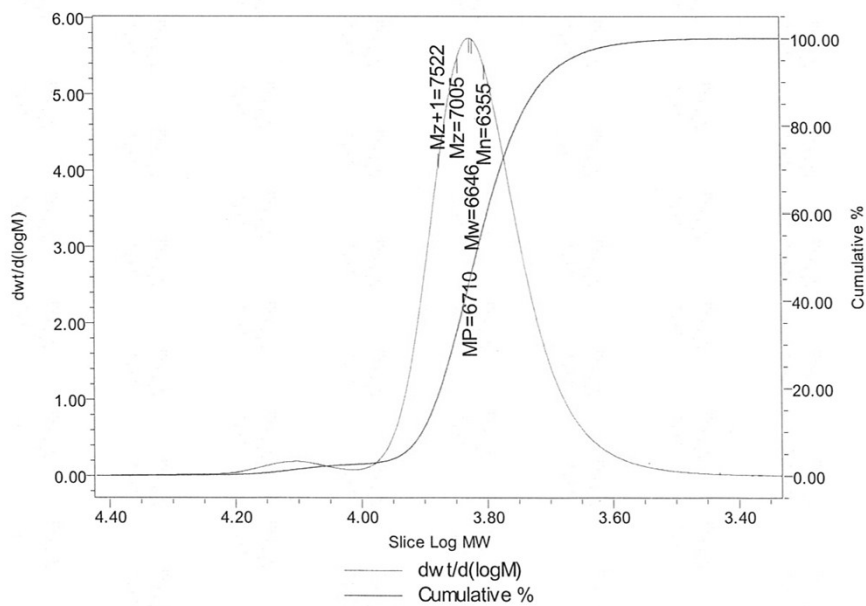
BAB 12000

Auto-Scaled Chromatogram



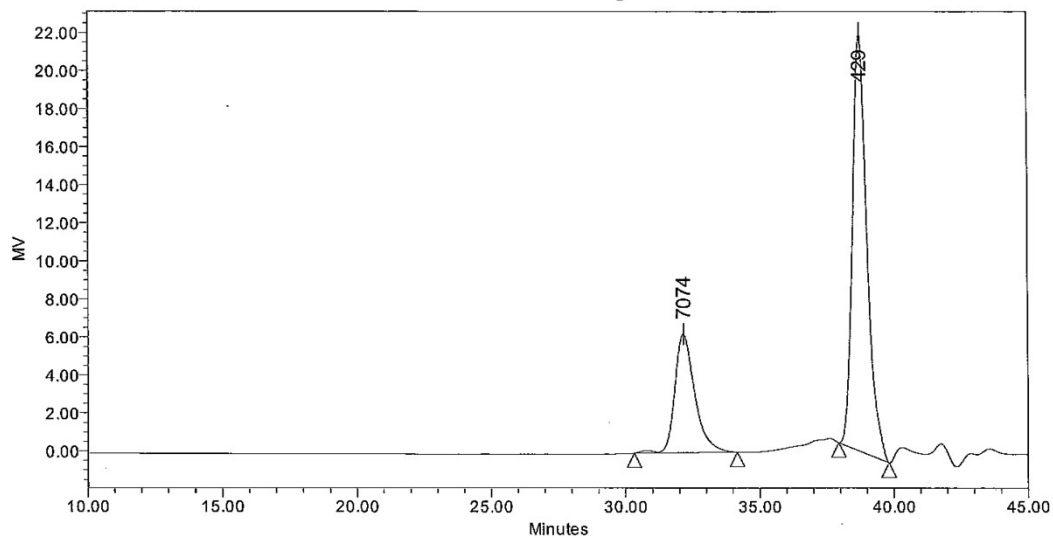
GPC Results

	Retention Time	Adjusted RT	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Baseline Start	Baseline End
1	32.106	32.106	6355	6646	6710	7005	7522	1.045814	29.133	34.733



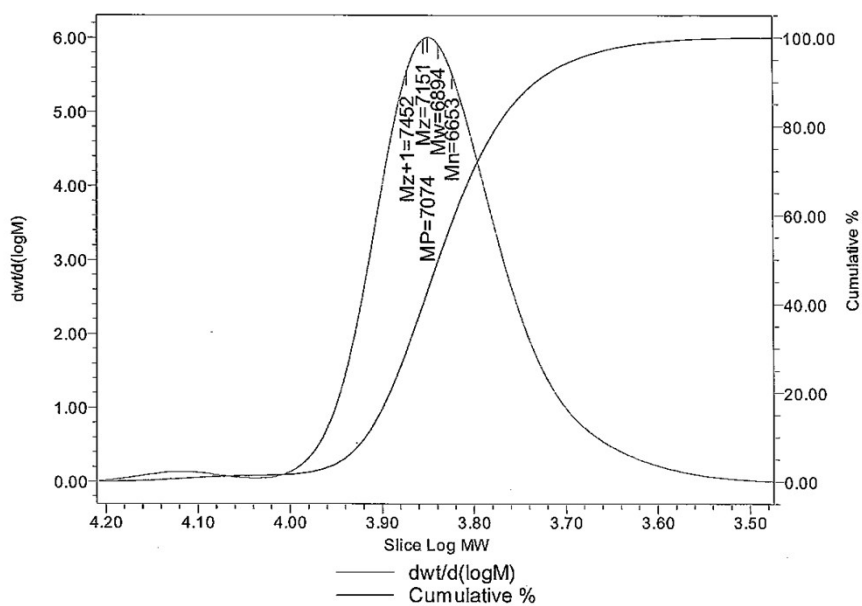
BAB 14000

Auto-Scaled Chromatogram

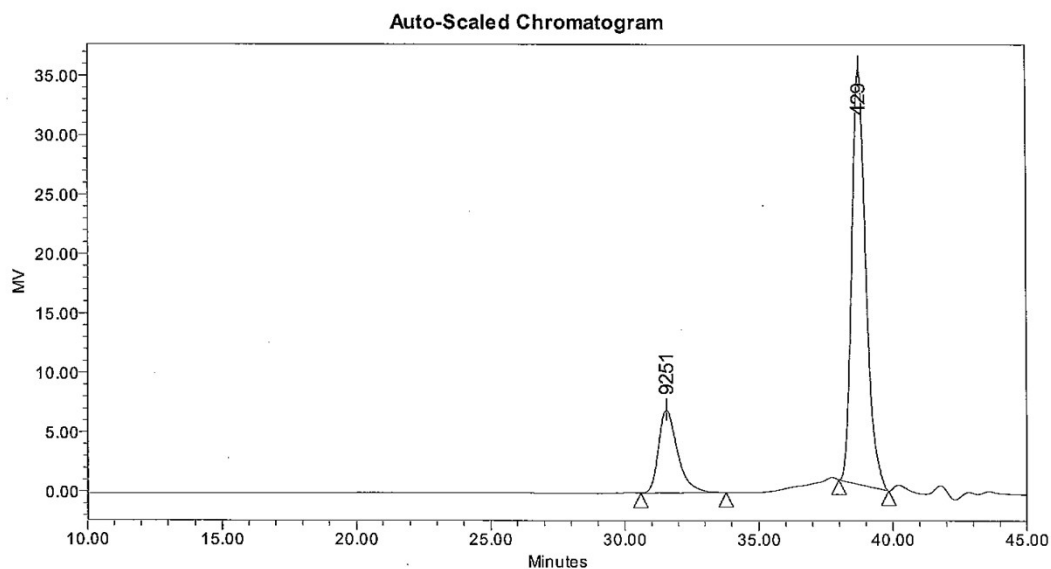


GPC Results

	Retention Time	Adjusted RT	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Baseline Start	Baseline End
1	32.164	32.164	6653	6894	7074	7151	7452	1.036256	30.333	34.167
2	38.752	38.752			429				37.950	39.817



BAB 17000



GPC Results

	Retention Time	Adjusted RT	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Baseline Start	Baseline End
1	31.561	31.561	8629	8878	9251	9102	9307	1.028817	30.600	33.783
2	38.752	38.752			429				37.983	39.850

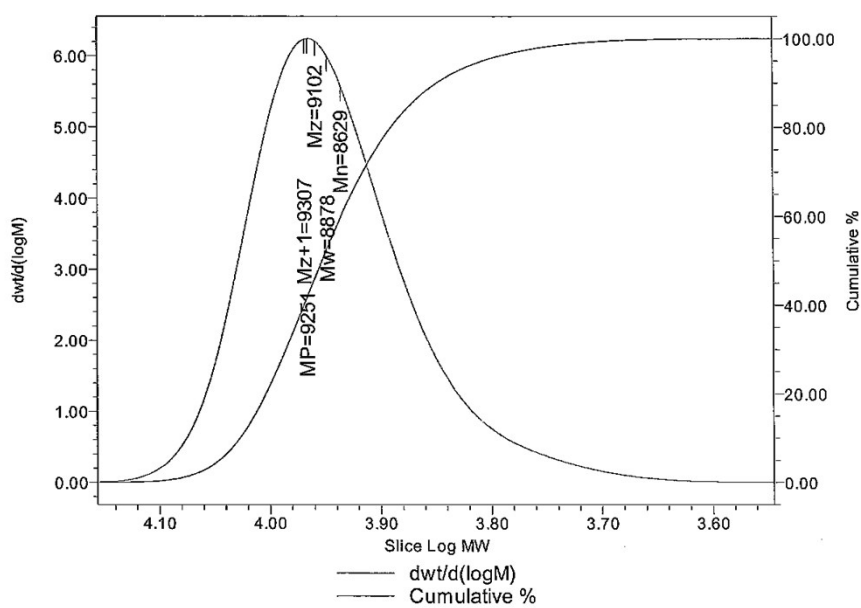


Figure 3S. GPC data of the BAB copolymers.

4. DSC

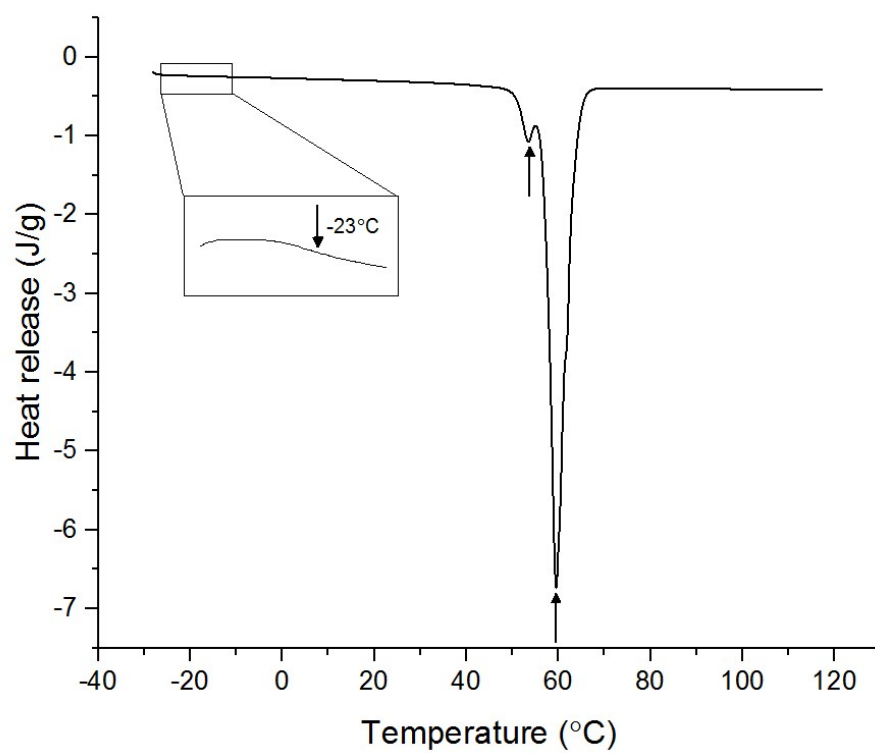


Figure 4S. DSC trace of the di-amino PEG starting material.

5. CMC and DLS

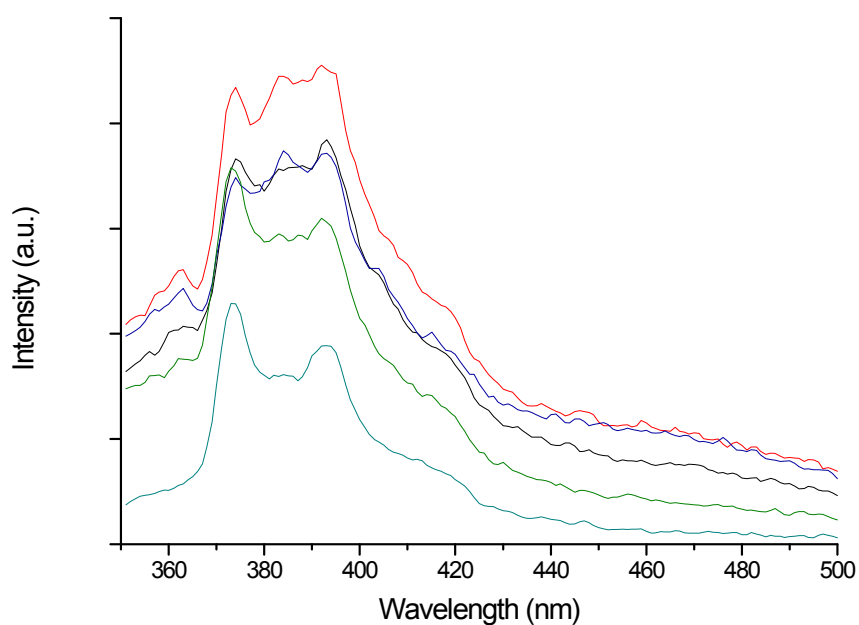


Figure 5S. Typical fluorescence spectra of pyrene in aqueous of BAB 12000 at various concentrations varying from 3.0×10^{-5} g/mL to 1.1×10^{-3} g/mL (increasing concentrations from top to bottom). For clarity only 5 representative curves for BAB 12000 are shown; all copolymers display similar curves.

Table 4S. Stock solution and minimum dilution concentrations achieved for the four block copolymers investigated.

BAB copolymer	Stock concentration (g mL ⁻¹)	Lowest concentration (g mL ⁻¹)
BAB 5000	2.10×10^{-3}	4.20×10^{-6}
BAB 12000	1.60×10^{-3}	13.2×10^{-6}
BAB14000	1.00×10^{-3}	1.00×10^{-7}
BAB 17000	1.06×10^{-3}	2.10×10^{-6}

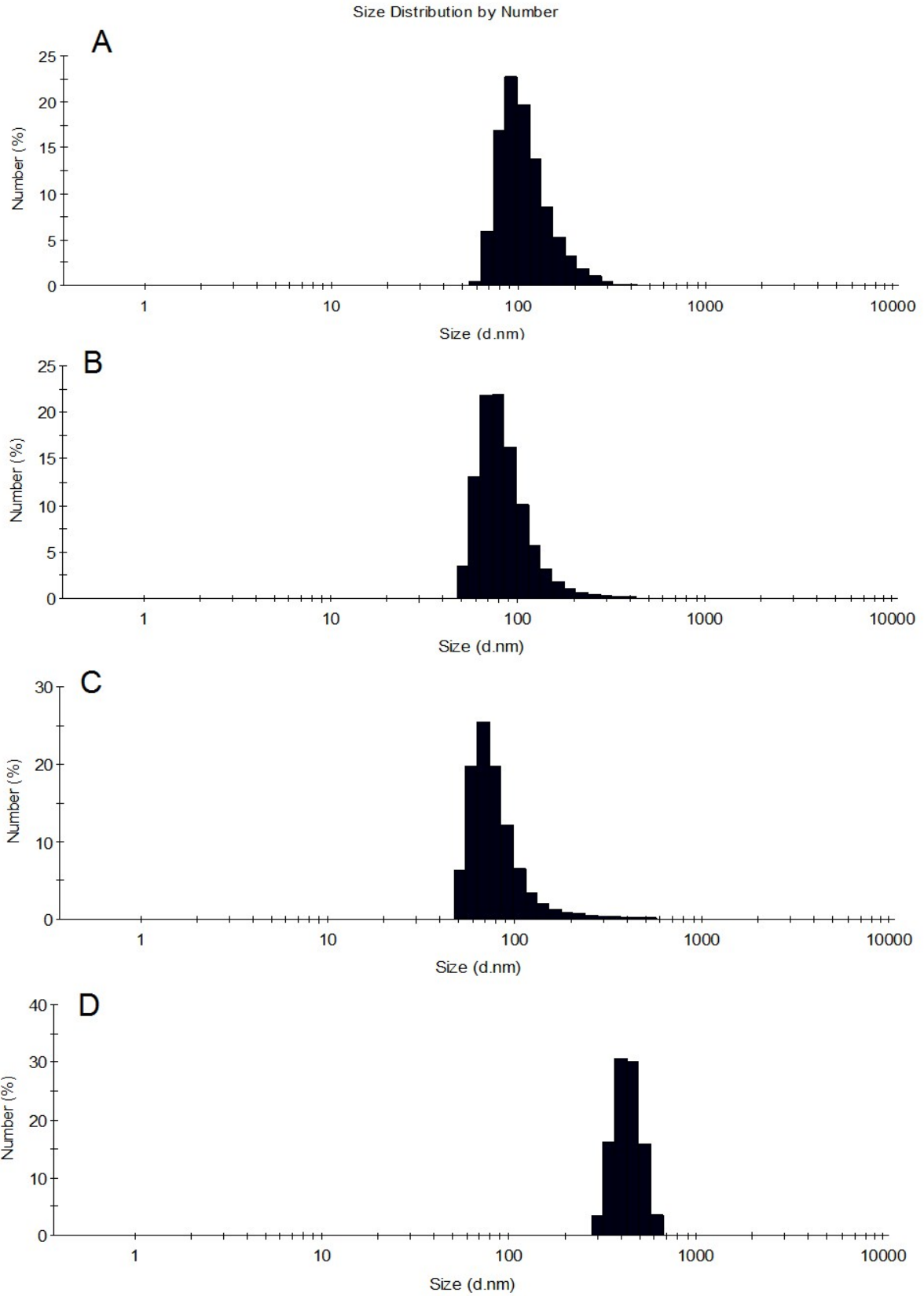


Figure 6S. DLS size distribution by number histograms of (A) BAB 5000, (B) BAB 12000, (C) BAB 14000 and (D) BAB 17000 micelles dialysed from acetone.

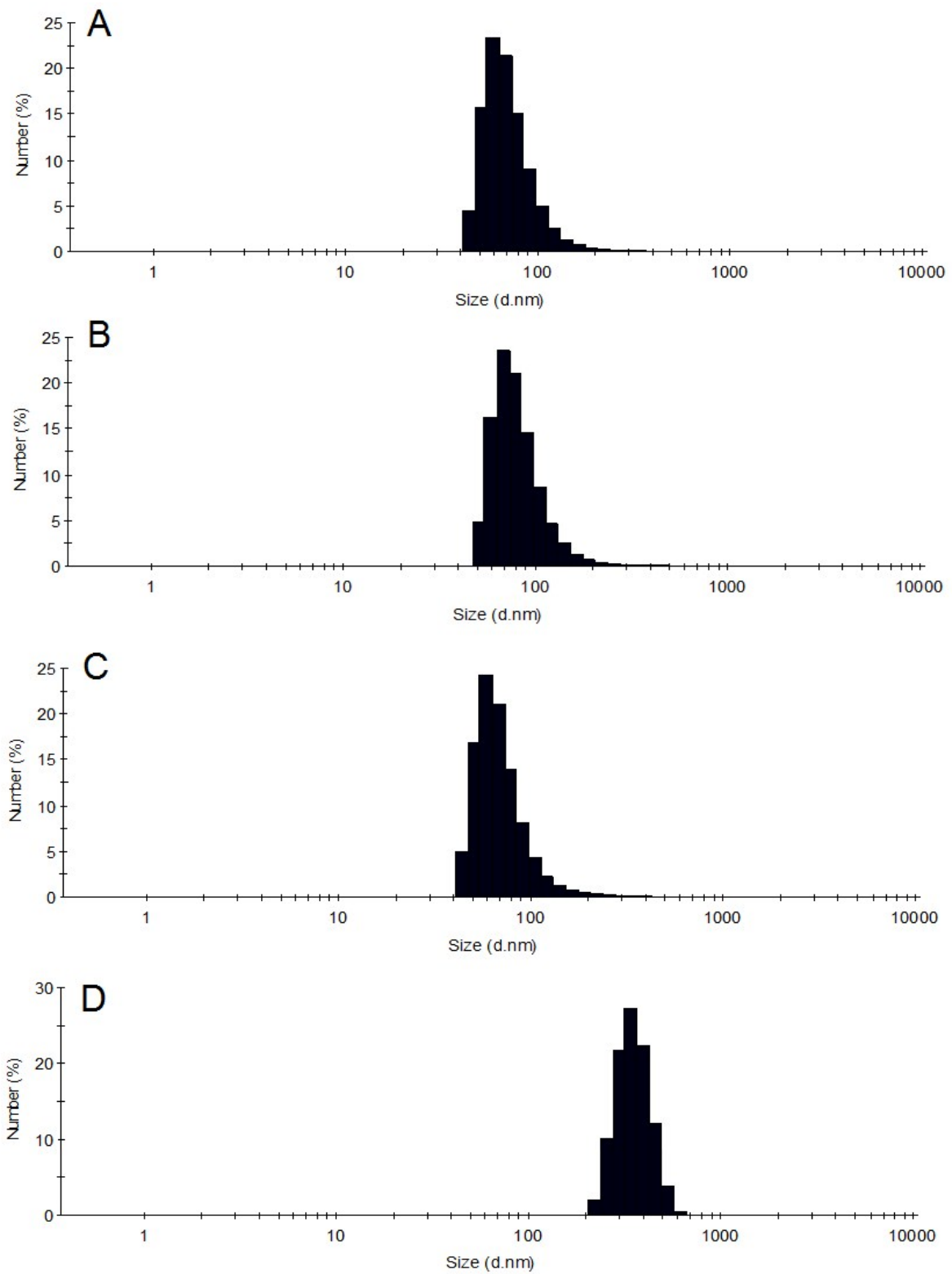


Figure 7S. DLS size distribution by number histograms of (A) BAB 5000, (B) BAB 12000, (C) BAB 14000 and (D) BAB 17000 micelles dialysed from DMSO.