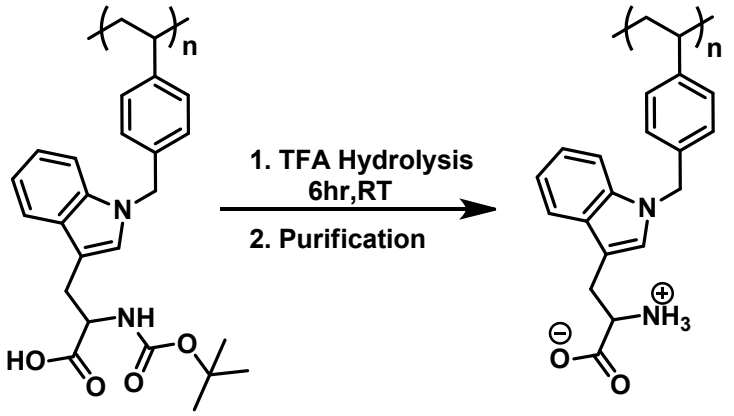
Electronic Supplementary Information

Tryptophan-Based Styryl Homopolymer and Polyzwitterions with Solvent-Induced UCST, Ion-Induced LCST and pH-Induced UCST

Somdeb Jana[§], Mahammad Anas[§], Tanmoy Maji, Sanjib Banerjee[‡] and Tarun K. Mandal*

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

Contents **Page No.**



Scheme S1. Synthesis of poly(TrpVBz) by the Boc deprotection of poly(Boc-TrpVBz)

Table S1. Effect of water percentage on the phase behaviour of poly(Boc-TrpVBz)$_{50}$ solution in different mixed solvents.

Organic solvent	**MWP (%) required for turbid suspension as examined via**		**Water percentage (%)**	**Cloud point (T_{cU}) (°C)**
	Transmittance	**DLS**		
DMSO	21.5	21.5	21	18.3
			23	34.5
			25	53.6
			27	72.3
DMF	27.5	28.0	27	19.4
			29	29.3
			31	40.0
			33	51.0
			35	31.5
			37	69.7
MeOH	11.5	11.5	10	12.2
			12	25.2
			14	39.5
			16	48.2
			18	56.6

Table S2. Effect of molecular weight of poly(Boc-TrpVBz) on its UCST-type cloud point (T_{cU}) in different mixed solvents.

Sample name	Cloud point (T_{cU}) (°C)		
	DMSO-Water (23% water)	DMF-Water (31% water)	MeOH-Water (12% water)
Poly(Boc-TrpVBz)$_{25}$	11.9	-	-
Poly(Boc-TrpVBz)$_{25}$	25.8	37.5	21.4
Poly(Boc-TrpVBz)$_{50}$	34.8	40.5	26.9
Poly(Boc-TrpVBz)$_{100}$	50.6	45.9	35.4

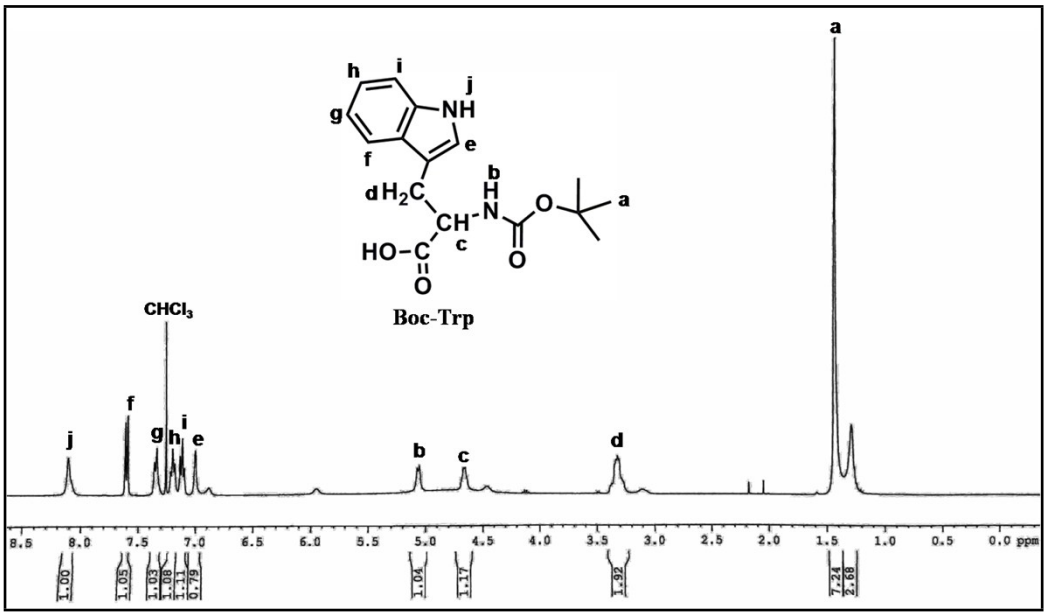


Figure S1. ^{1}H-NMR spectrum of Boc-Trp (The signal at δ 7.26 ppm corresponds to $CHCl_3$ present in $CDCl_3$).

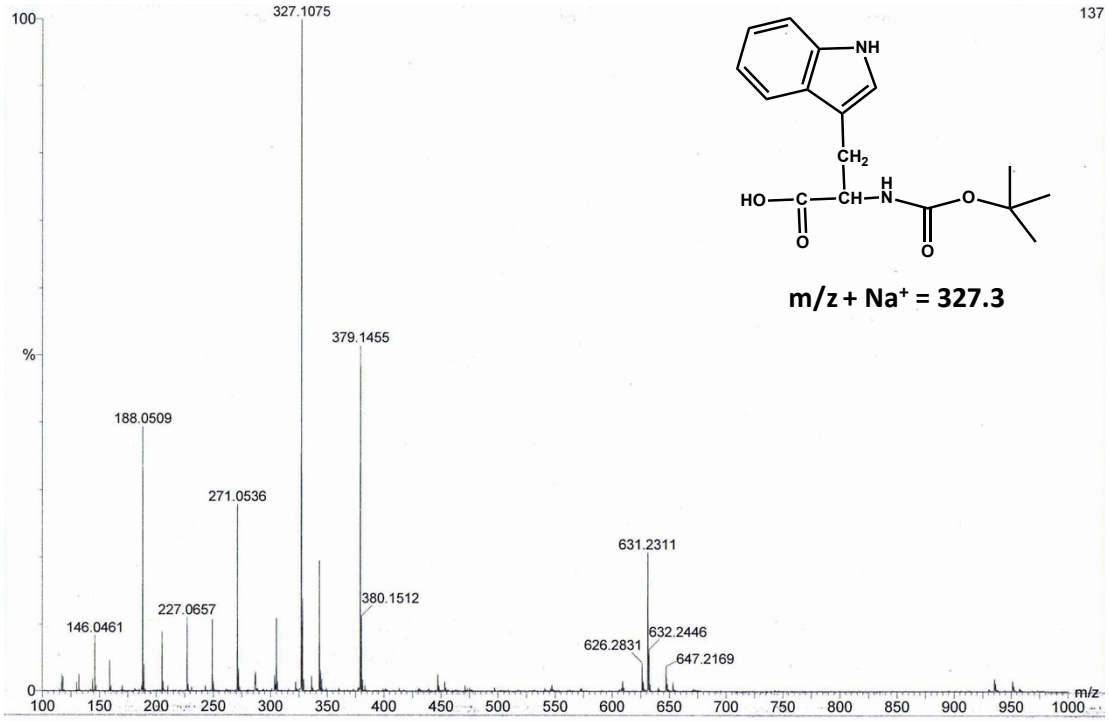


Figure S2. ESI-MS spectrum of Boc-Trp (theoretical m/z + Na^+ = 327.3)

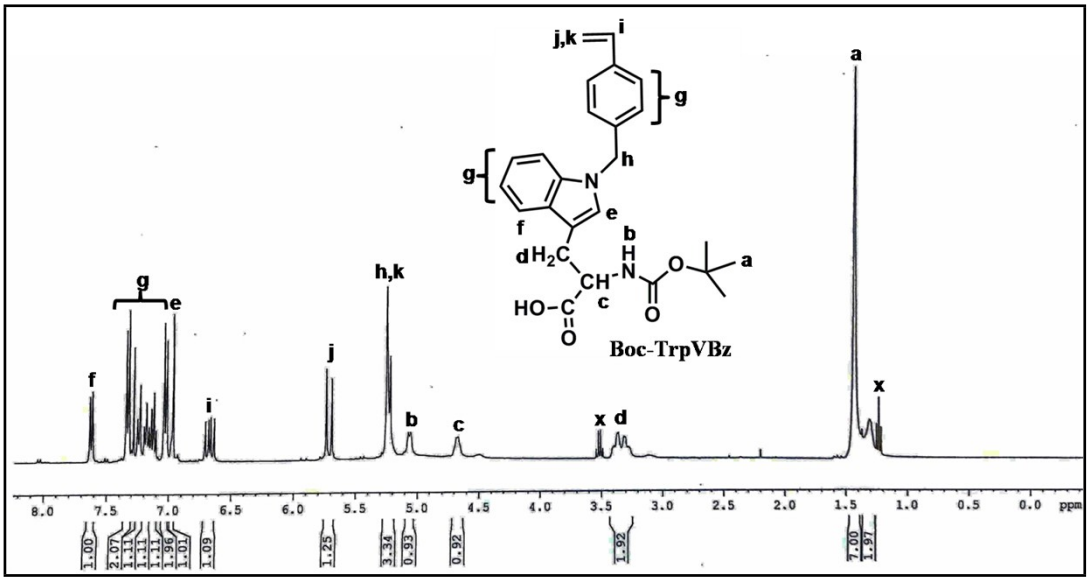


Figure S3. ^{1}H-NMR spectrum of Boc-TrpVBz (The signal at 'x' for diethyl ether).

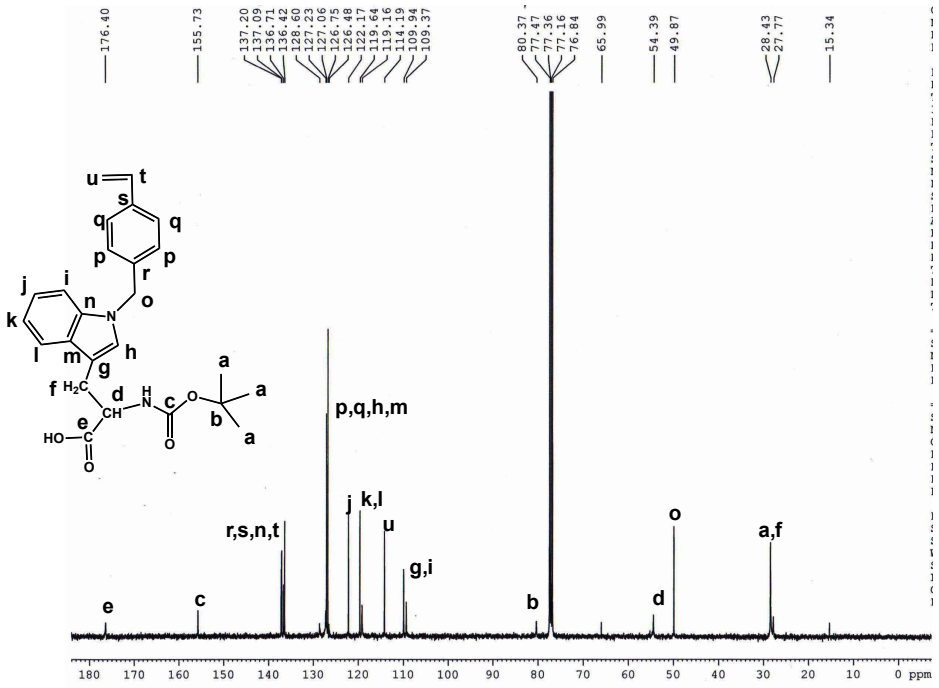


Figure S4. ^{13}C-NMR spectrum of Boc-TrpVBz.

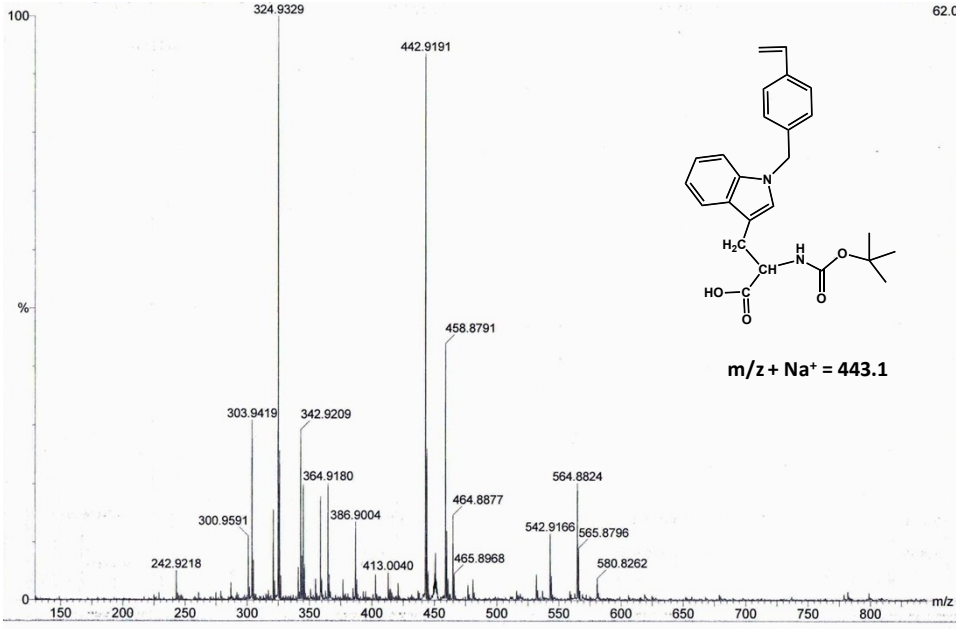


Figure S5. ESI-MS spectrum of Boc-TrpVBz (theoretical m/z + Na^+ = 443.1).

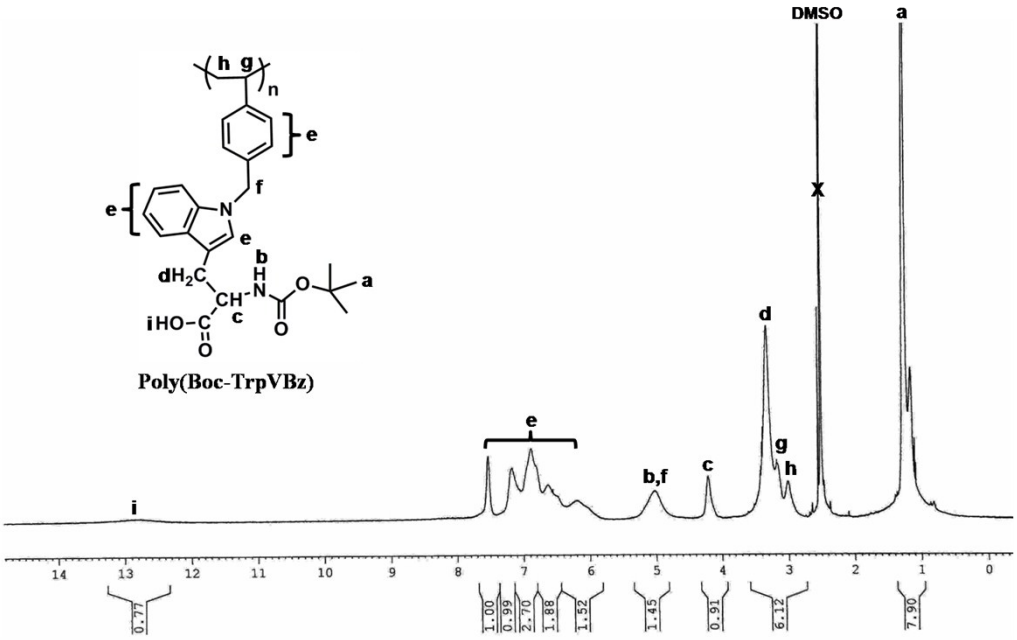


Figure S6. ^{1}H-NMR spectrum of poly(Boc-TrpVBz) in DMSO-d_6.

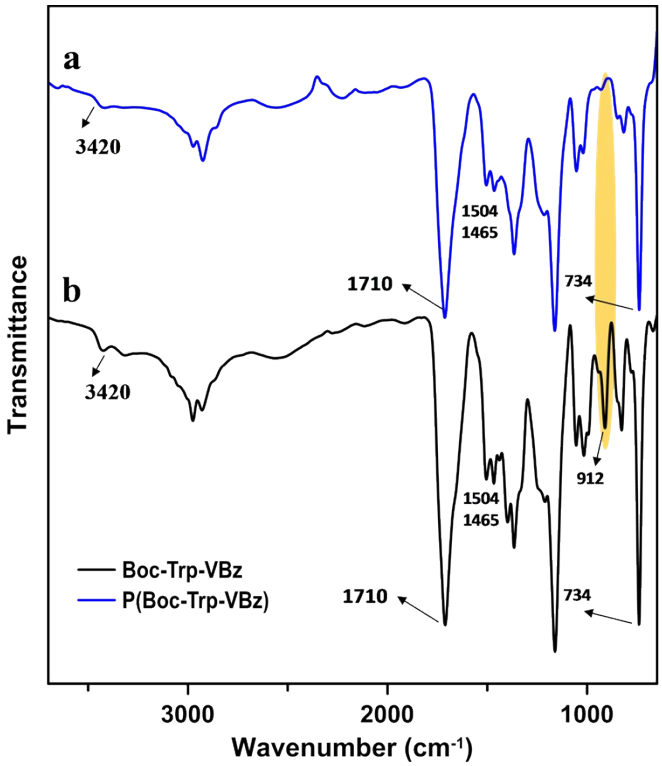


Figure S7. FTIR spectra of poly(Boc-TrpVBz) and Boc-TrpVBz monomer

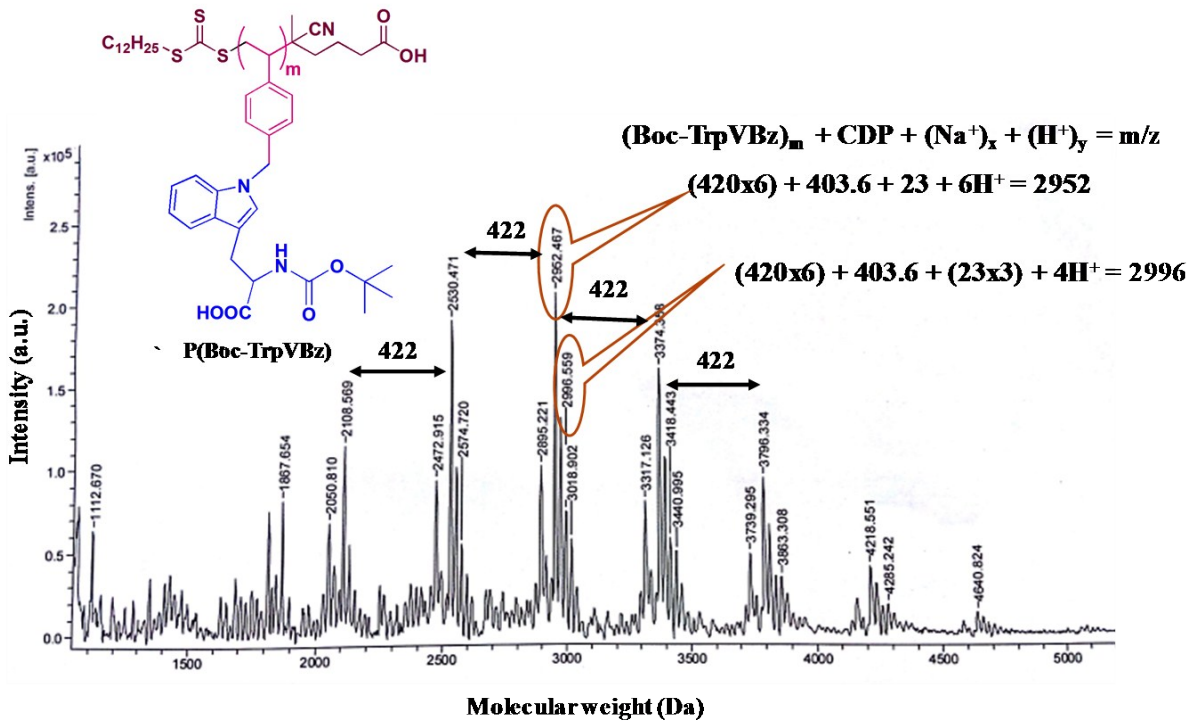


Figure S8. MALDI-TOF-MS spectrum of poly(4-vinyl benzyl [Boc-tryptophan])$_8$ [poly(Boc-TrpVBz)$_8$].

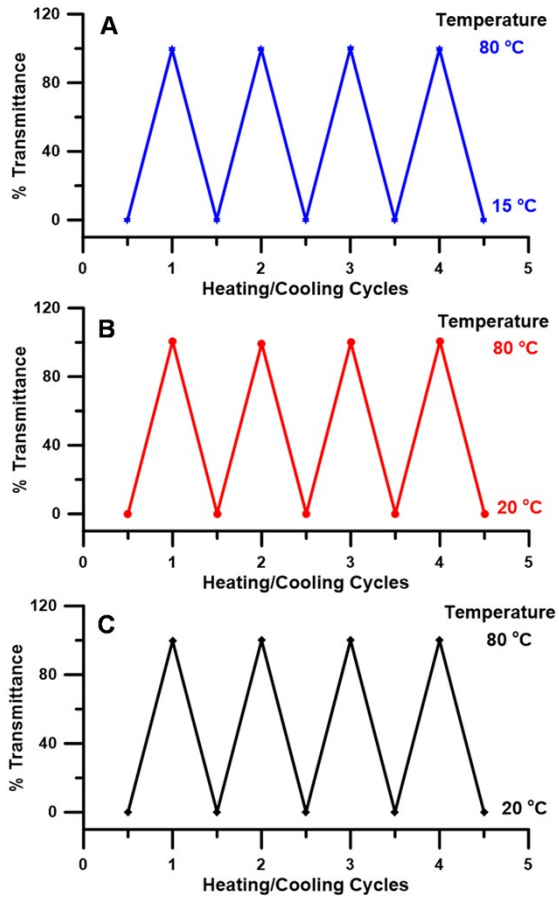

A
Temperature
80 °C
15 °C
% Transmittance
120
80
40
0
0
1
2
3
4
5
Heating/Cooling Cycles
B
Temperature
80 °C
20 °C
% Transmittance
120
80
40
0
0
1
2
3
4
5
Heating/Cooling Cycles
C
Temperature
80 °C
20 °C
% Transmittance
120
80
40
0
0
1
2
3
4
5
Heating/Cooling Cycles

Figure S9. Variation of % transmittance of solutions of poly(Boc-TrpVBz)$_{50}$ (0.5 wt%) in different mixed solvents under four heating/cooling cycles: (A) MeOH-water (12%); (B) DMSO-water (31%) and (C) DMF-water (31%).

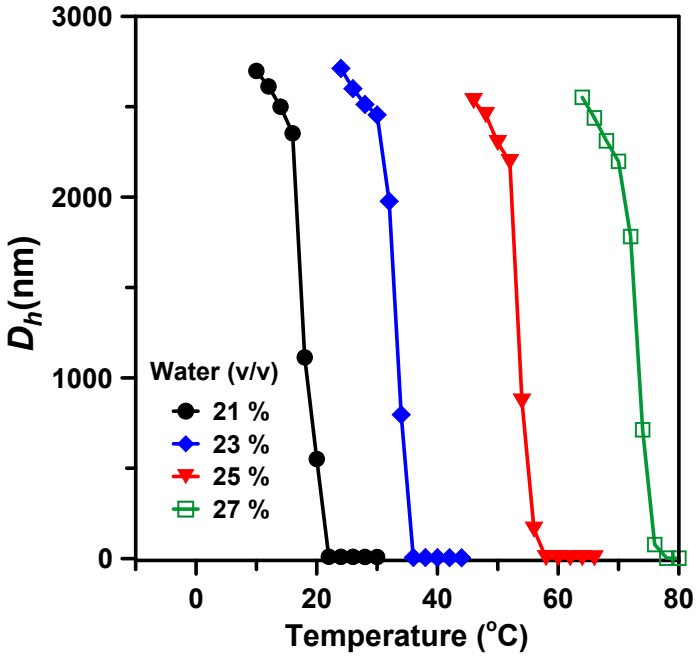


Figure S10. Variation of hydrodynamic diameter (D_h) with temperature for poly(Boc-TrpVBz)$_{50}$ (0.5 wt%) in DMSO-water mixed solvent of varying water content.

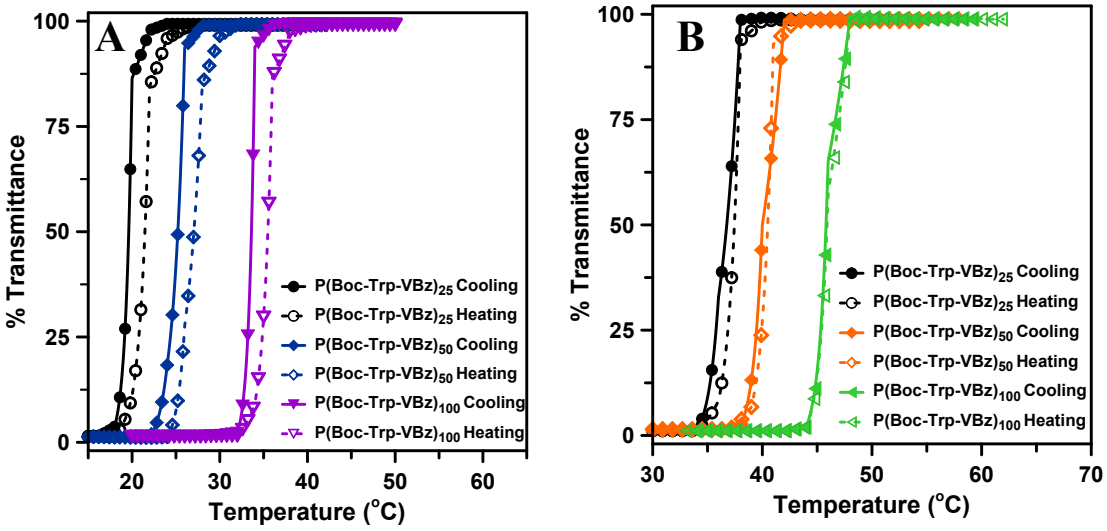


Figure S11. Turbidity curves (at λ = 600 nm) of poly(Boc-TrpVBz) of different molecular weights in (A) MeOH-Water (12 %) and (B) DMF-water (31 %).

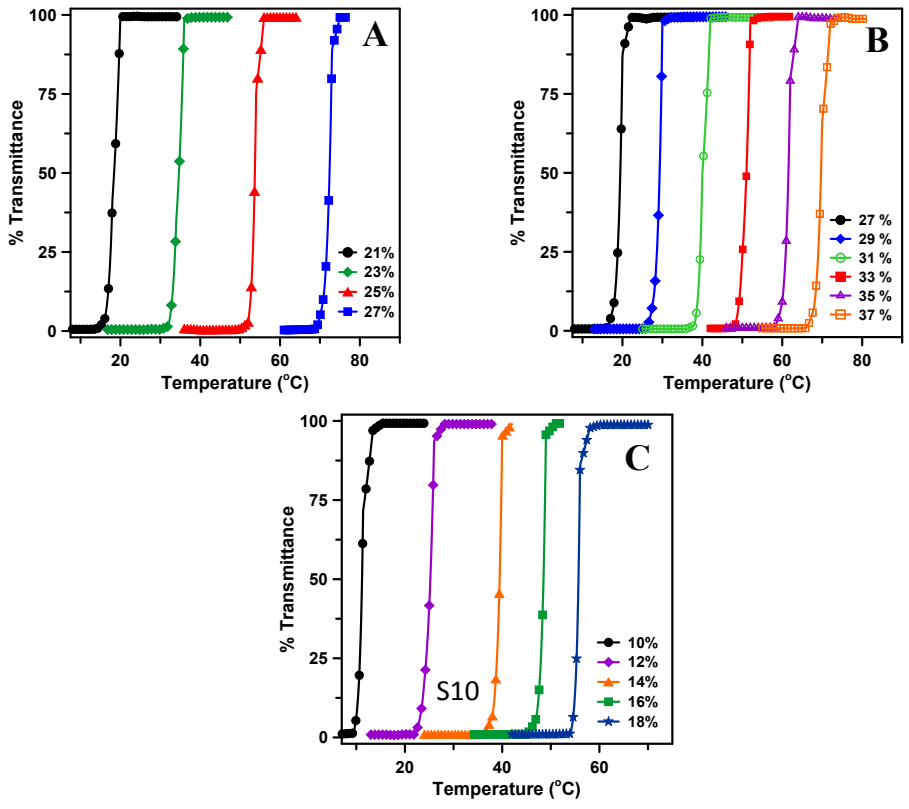


Figure S12. Turbidity curves (at $\lambda = 600$ nm) of poly(Boc-TrpVBz)$_{50}$ (0.5 wt%) with the variation of water percentage in mixed solvent containing (A) DMSO, (B) DMF and (C) MeOH.

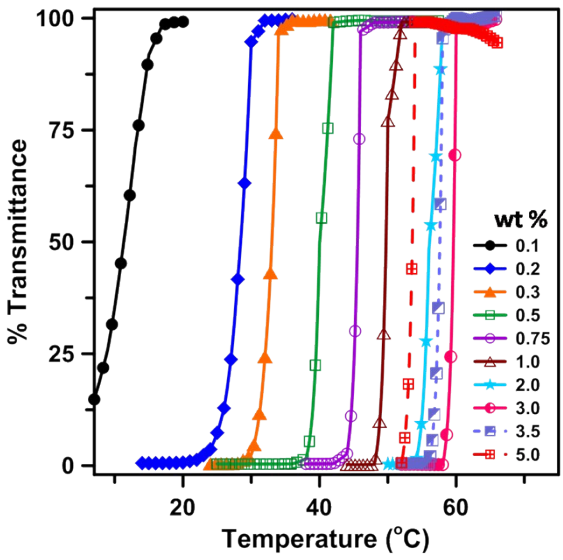


Figure S13. Turbidity curves for varying concentration of poly(Boc-TrpVBz)$_{50}$ in DMF-water (31 %) mixed solvent.

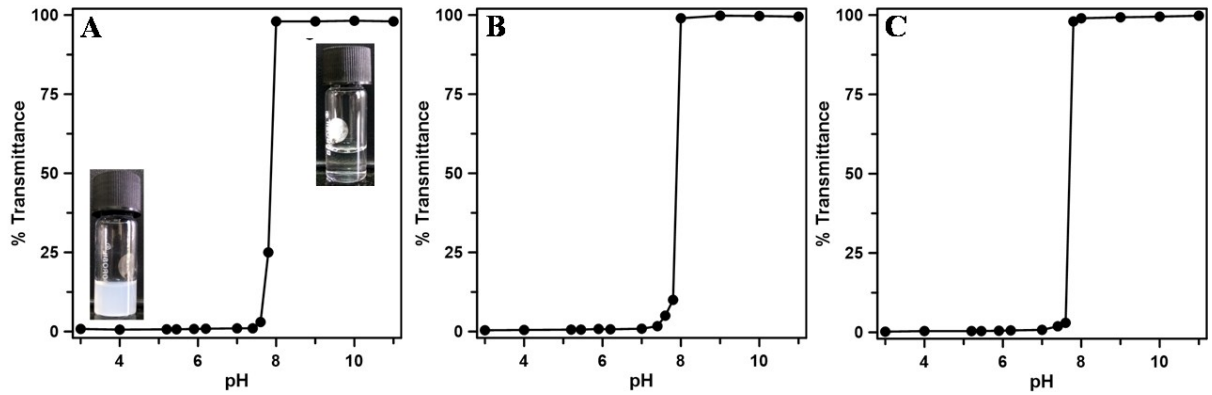


Figure S14. The plot of % transmittance (at λ = 600 nm) of 0.5 wt % aqueous solutions of poly(Boc-TrpVBz)s of different molecular weights at different pHs: (A) poly(Boc-TrpVBz)$_{25}$; (B) poly(Boc-TrpVBz)$_{50}$ and (C) poly(Boc-TrpVBz)$_{100}$. Inset showed the photographs of aqueous poly(Boc-TrpVBz)$_{25}$ solution at different pHs.

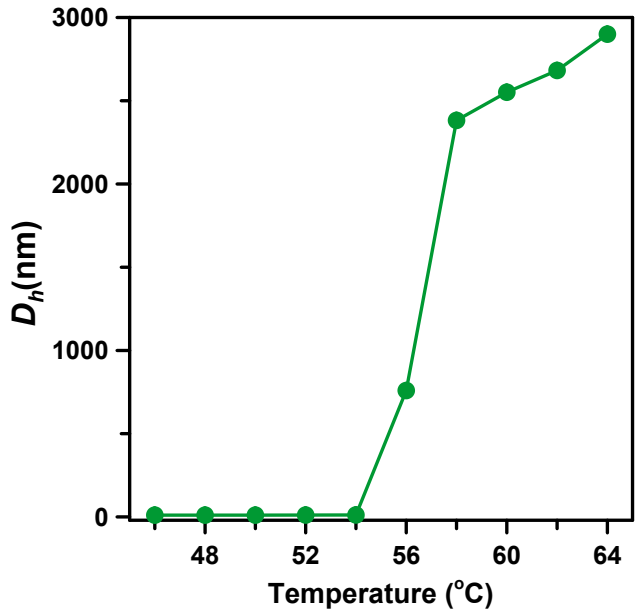


Figure S15. Variation of hydrodynamic diameter (D_h) with temperature for aqueous poly(Boc-TrpVBz)$_{100}$ solution at pH 8.5 in presence of 90 mM of Bu_4NBr.

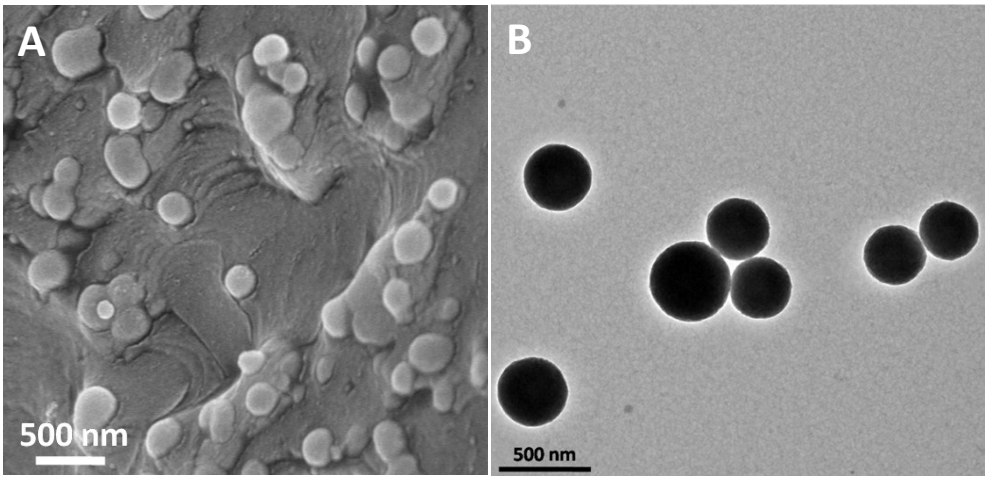


Figure S16. (A) FESEM and (B) TEM images of the aqueous solution of poly(Boc-TrpVBz)$_{50}$ (0.5wt%) in the presence of 90 mM Bu_4NBr at pH 8.5.

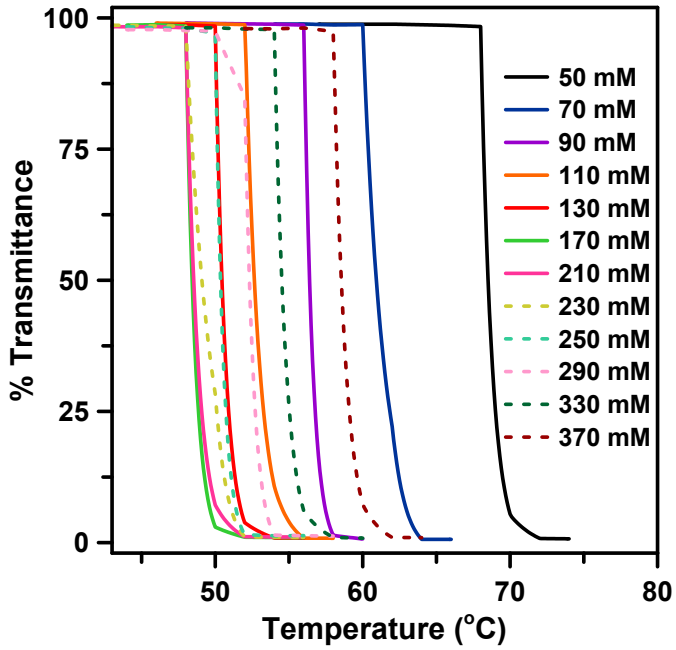


Figure S17. % Transmittance versus temperature curves for aqueous poly(Boc-TrpVBz)$_{100}$ solution at pH 8.5 in presence of varying concentrations of Bu_4NBr.

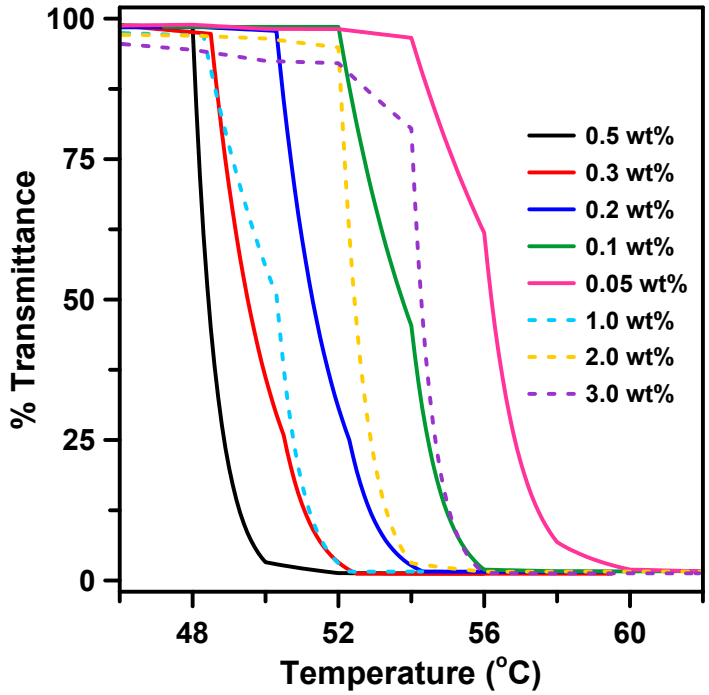


Figure S18. % Transmittance versus temperature curves of varying concentrations of aqueous poly(Boc-TrpVBz)$_{100}$ solution at pH 8.5 in presence of 170 mM of Bu_4NBr.

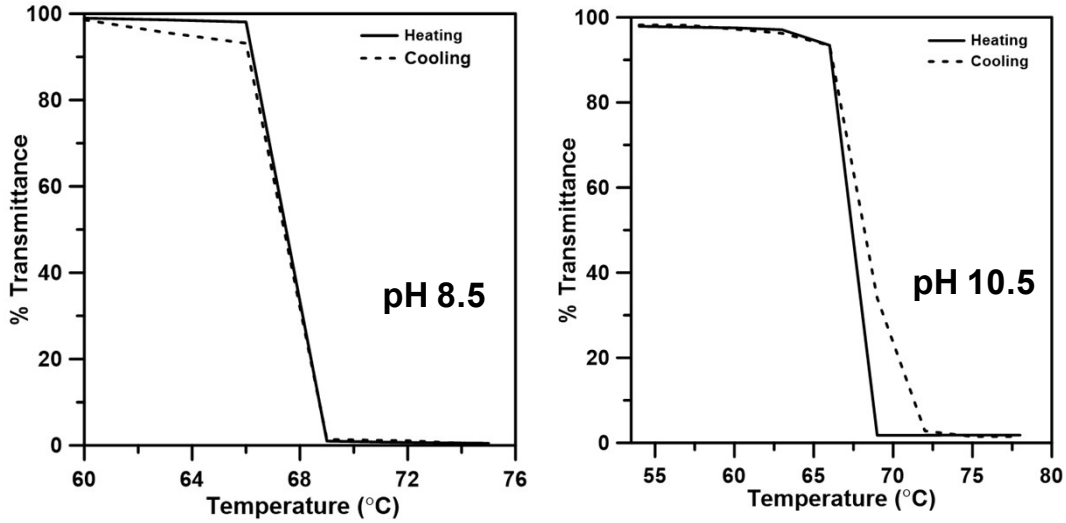


Figure S19. Turbidity curves (heating/cooling) of aqueous solutions of poly(Boc-TrpVBz)$_{50}$ (0.5 wt%) in the presence of 90 mM Bu_4NBr at different pHs.

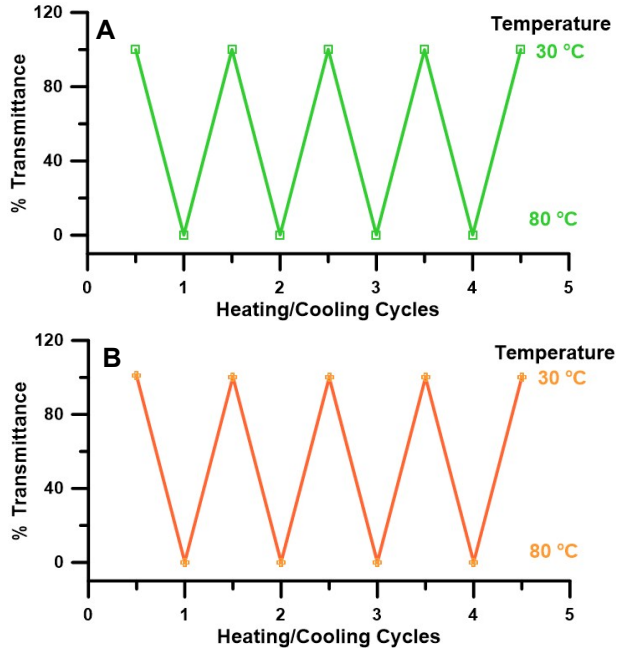


Figure S20. Variation of % transmittance of aqueous solutions of poly(Boc-TrpVBz)$_{50}$ (0.5 wt%) in the presence of 90 mM Bu_4NBr under four heating/cooling cycles at different pHs: (A) 8.5 and (B) 10.5.

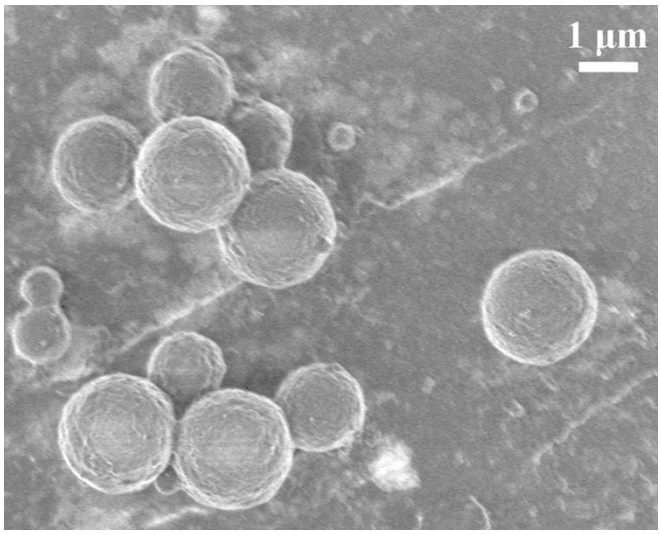


Figure S21. FESEM image of the aqueous turbid suspensions of poly(TrpVBz)$_{50}$ (0.5 wt%).