Electronic Supplementary Information (ESI)

Short oligo(ethylene glycol) chain incorporated thermoresponsive

microgels: from structural analysis to modulation of solution properties

Priyanshi Agnihotri,^a Ritu Raj,^b Dinesh Kumar,^b Abhijit Dan*a

^a Department of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University

- Chandigarh, Sector 14, Chandigarh 160014, India

^b Centre of Biomedical Research (CBMR), SGPGIMS Campus, Raibareli Road, Lucknow-226014, Uttar Pradesh, India

Corresponding author

*Email: abhijit@pu.ac.in (A. Dan)

Microgel	Code	NIPAM:	NIPAM (g)	BIS (g)	OEGMA (g)
C		BIS:			
		OEGMA			
		(mol%)			
PNIPAM	MG^5	95: 5: 0	1.630	0.117	0
PNIPAM-co- MEMA	MG_{M1}^{5}	94: 5: 1	1.612	0.117	0.022
	MG_{M5}^{5}	90: 5: 5	1.546	0.117	0.109
	MG_{M10}^{1}	89: 1: 10	1.532	0.023	0.218
	MG_{M10}^{5}	85: 5: 10	1.461	0.117	0.218
	$MG_{M10}^{\ 10}$	80: 10: 10	1.374	0.234	0.218
PNIPAM-co- DEGMA	MG_{D1}^{5}	94: 5: 1	1.612	0.117	0.028
	MG_{D5}^{5}	90: 5: 5	1.546	0.117	0.143
	MG_{D10}^{1}	89: 1: 10	1.532	0.023	0.285
	MG_{D10}^{5}	85: 5: 10	1.461	0.117	0.285
	$MG_{D10}^{\ 10}$	80: 10: 10	1.374	0.234	0.285
PNIPAM-co- PEGMA ₃₀₀	MG_{P1}^{5}	94: 5: 1	1.612	0.117	0.046
	MG_{P5}^{5}	90: 5: 5	1.546	0.117	0.217
	MG_{P10}^{1}	89: 1: 10	1.532	0.023	0.455
	MG_{P10}^{5}	85: 5: 10	1.461	0.117	0.455
	MG_{P10}^{10}	80: 10: 10	1.374	0.234	0.455

Table S1 Reaction Compositions for the Synthesis of Microgels*

*The superscripts and subscripts in the microgel codes represent the amount of crosslinker and comonomer

in mol%, respectively added during the synthesis with M = MEMA, D = DEGMA and $P = PEGMA_{300}$.



Fig. S1 Normalized field autocorrelation function for PNIPAM microgels (5 mol% crosslinker) at a concentration of 5 × 10⁻⁴ g/ml measured at 25 °C and θ = 90°. Solid line represents the cumulant fit.

Table S2 Exponential Decay Equations used for Curve Fits in Origin

Function	Equation		
Mono-exponential	$y = ae^{-bx}$		
Bi-exponential	$y = ae^{-bx} + ce^{-dx}$		

a, b, c and d are the coefficients of independent variable (x).

For mono-exponential decay rates T₂ were calculated as follows:

$$T_2 = \frac{1}{b} \tag{S1}$$

For bi-exponential decay rates $T_2^{Short}(T_{2S})$, $T_2^{Long}(T_{2l})$ were calculated as follows:

$$T_{2s} = \frac{1}{b}$$

$$T_{2l} = \frac{1}{d}$$
(S2)
(S3)



Fig. S2 Particle size distribution histogram of (a) PNIPAM (b) PNIPAM-co-MEMA (c) PNIPAM-co-DEGMA (d) PNIPAM-co-PEGMA₃₀₀ microgels (5 mol% crosslinker, 10 mol% comonomer where applicable) obtained from TEM images.

Table S3 Average Size of the Microgels Obtained from TEM Results*

Microgels	Diameter (nm)
PNIPAM	256 ± 20
PNIPAM-co-MEMA	313 ± 39
PNIPAM-co-DEGMA	452 ± 48
PNIPAM-co-PEGMA ₃₀₀	547 ± 52

* The crosslinker content = $5 \mod \%$ and the comonomer feed = $10 \mod \%$ (where applicable).



Fig. S3 Effective volume fraction (Φ_{eff}) as a function of mass concentration for (a) PNIPAM, (b) PNIPAM-co-MEMA, (c) PNIPAM-co-DEGMA and (d) PNIPAM-co-PEGMA₃₀₀ microgels (5 mol% crosslinker, 10 mol% comonomer where applicable) measured at different temperatures.