Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information for

STRUCTURE-RELATED DIFFERENCES IN THE TEMPERATURE-REGULATED FLUORESCENCE RESPONSE OF LCST TYPE POLYMERS

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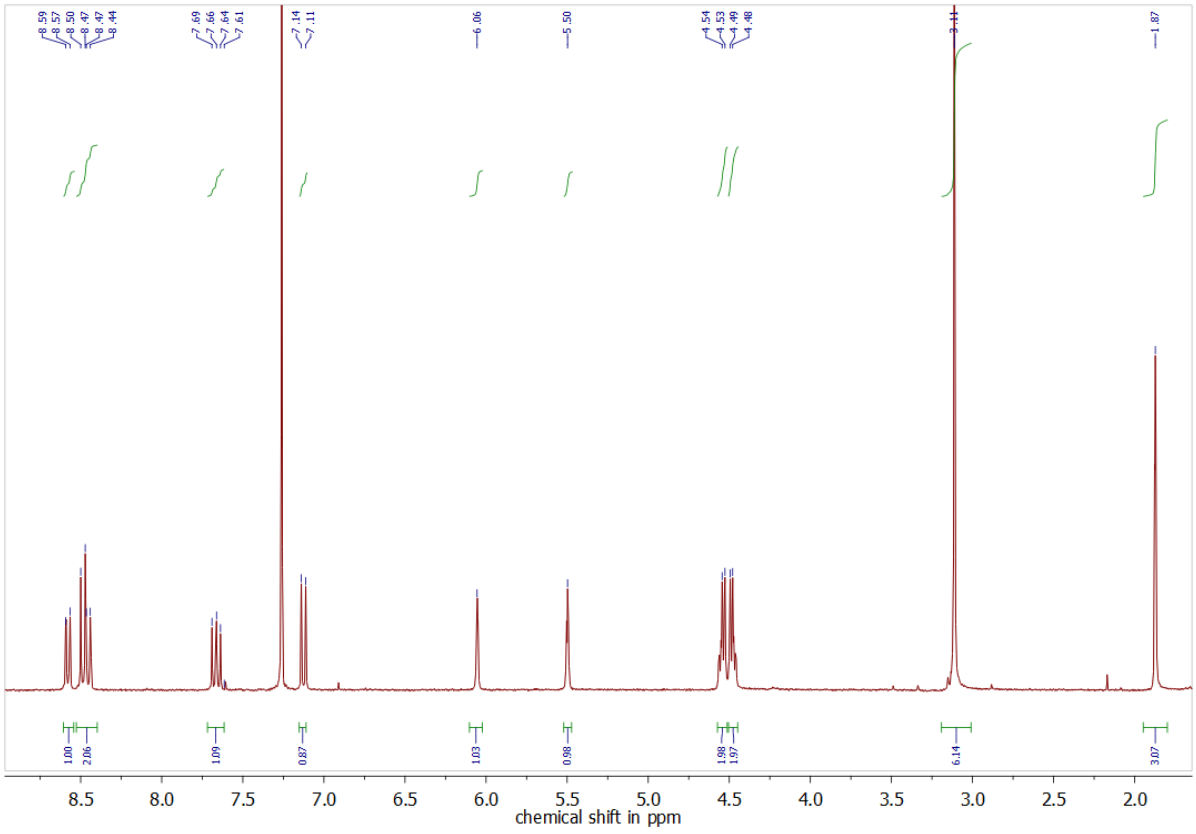
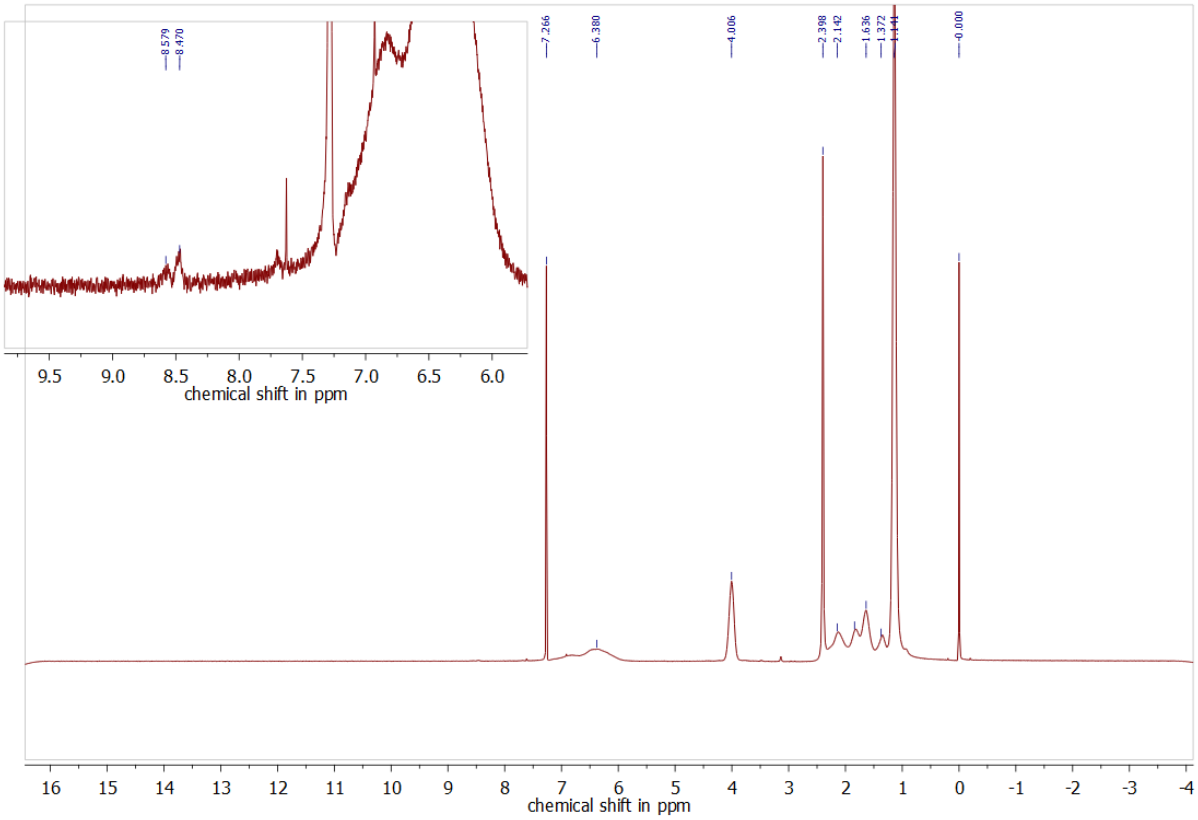
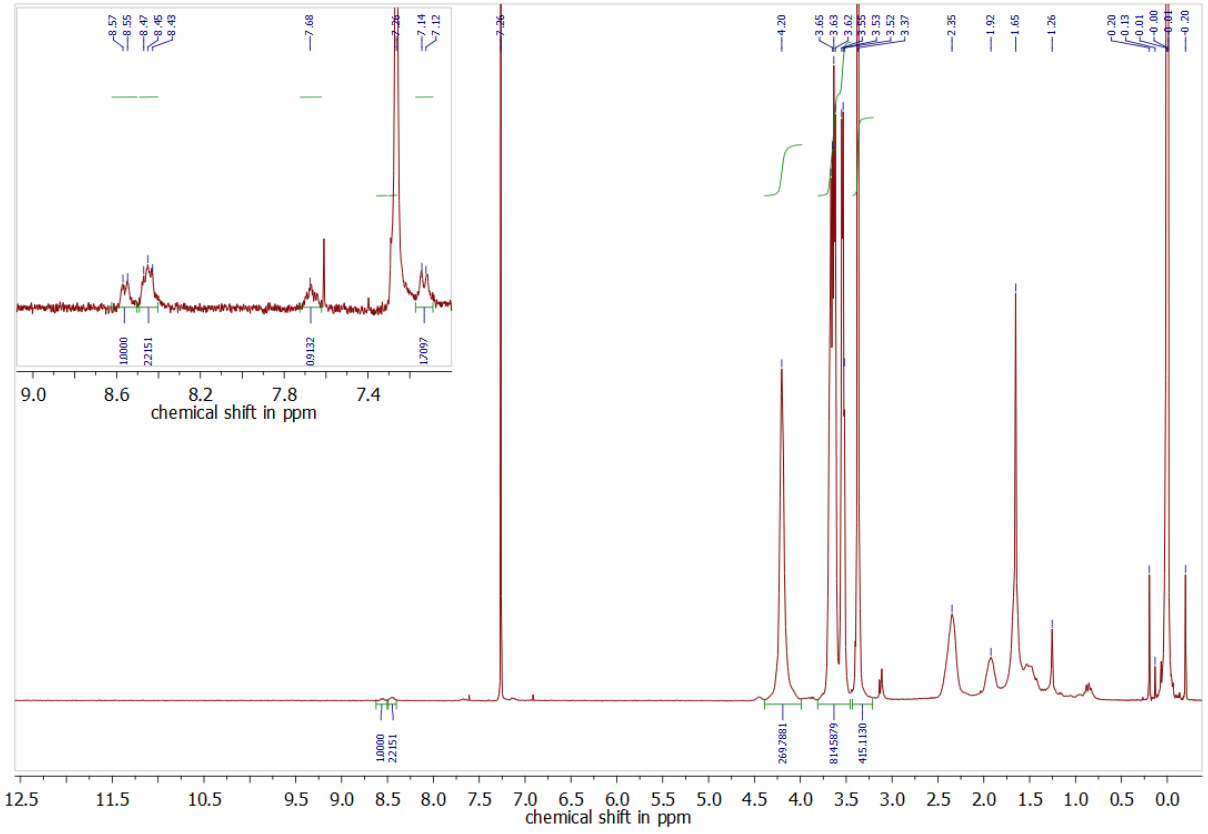
a)



b)


8.579
8.470
7.266
6.380
4.006
2.398
2.142
1.636
1.372
1.141
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0
chemical shift in ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
chemical shift in ppm

c)


8.57
8.55
8.47
8.45
8.43
7.68
7.26
7.14
7.12
10000
22151
09132
12097
9.0 8.6 8.2 7.8 7.4
chemical shift in ppm
7.26
4.20
3.65
3.63
3.62
3.55
3.53
3.52
3.37
2.35
1.92
1.65
1.26
0.20
0.13
0.01
0.00
0.01
0.20
10000
22151
269.7881
814.5879
415.1130
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift in ppm

d)

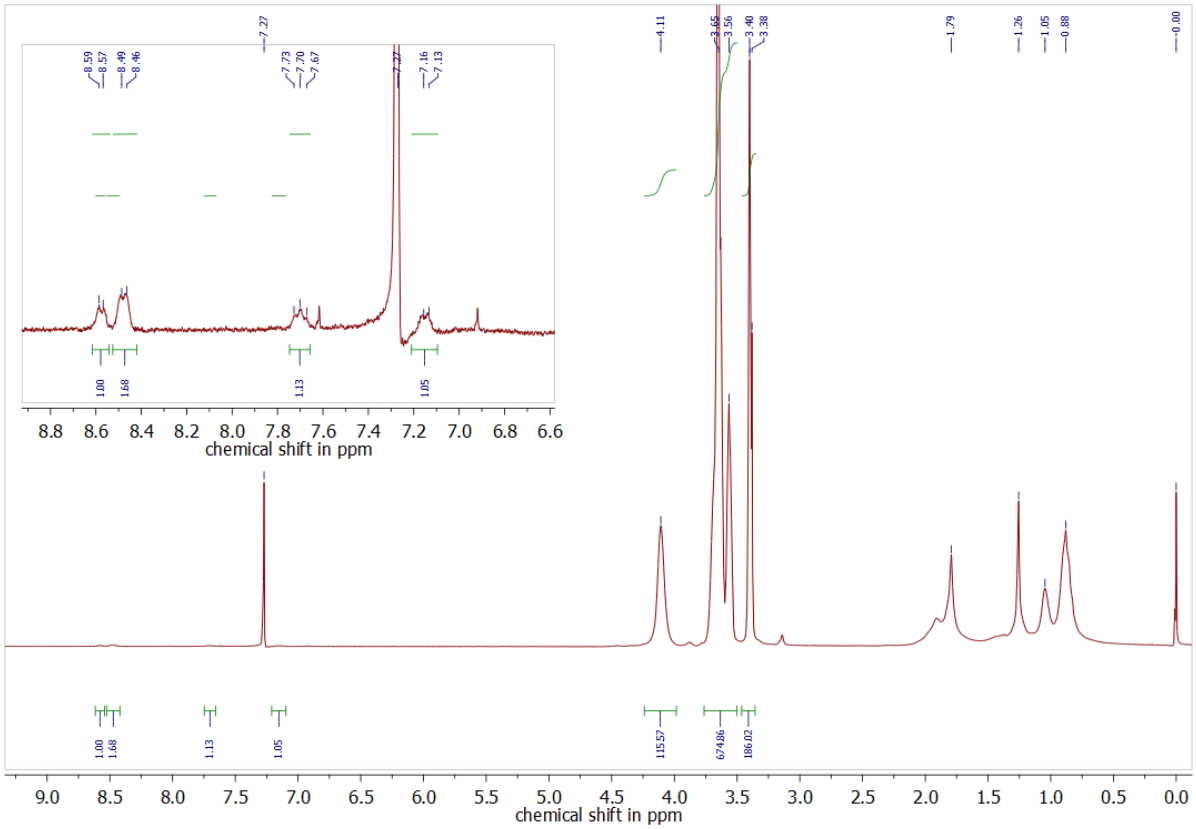


Fig. S1. ^{1}H-NMR spectrum of **a)** 4-DMN bearing monomer (**3**), **b)** labeled pNIPAm (**P-1**), **c)** labeled pMEO_2A (**P-2**), and **d)** labeled p(MEO_2MA-co-OEGMA) (**P-3**) in $CDCl_3$.

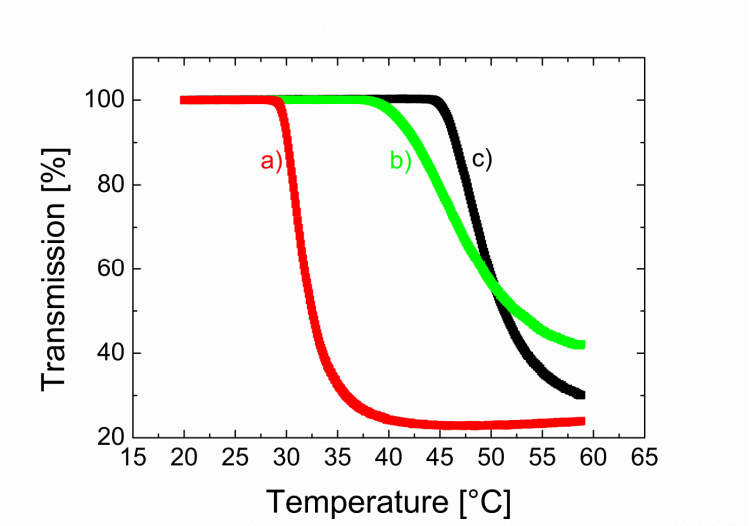


Fig. S2. Transmission-temperature profile of **a) P-1**, **b) P-2**, and **c) P-3** in PBS at a concentration of 0.1 g/L.

Table S1. The photophysical characterization of 4-DMN labeled monomer (**3**) dissolved in various solvents (δ_t: Hansen solubility parameter of solvents at 25 °C, δ_d, δ_p, and δ_h: the dispersive, polar and the hydrogen-bonding term of δ_t, respectively, λ^{abs}_{max}: wavelength of maximum absorbance, λ^{PL}_{max}: wavelength of maximum emission intensity, φ: steady-state fluorescence quantum yield, τ: fluorescence lifetime)

Solvent	δ_t [a)]	δ_d	δ_p	δ_h	λ^{abs}_{max} [nm]	λ^{PL}_{max} [nm]	φ [%]	τ [ns]
Hexane	14.9	14.9	0.0	0.0	391	459.5	61.0	6.9
Tetrachlorocarbon	17.8	17.8	0.0	0.6	400	476.5	70.0	7.0
Diethylene glycol dimethyl ether	18.0 [b)]	15.7 [b)]	6.1 [b)]	6.5 [b)]	415	522.0	12	2.4
Toluene	18.2	18.0	1.4	2.0	406	492.5	65.0	7.7
Chloroform	19.0	17.8	3.1	5.7	418	506.5	70.0	9.0
Acetone	20.1	15.5	10.4	7.0	415	526.0	3.6	3.0
Acetic Acid	21.3	14.5	8.0	13.5	424	539.0	2.6	3.2
Acetonitrile	24.6	15.3	18.0	6.1	419	532.0	4.0	2.8
Dimethylformamide	25.0	14.3	11.9	16.6	423	532.5	1.5	7.8
Dimethylsulfoxide	26.6	18.4	16.4	10.2	437	546.0	1.9	7.4
Ethanol	26.6	15.8	8.8	19.4	420	536.5	1.9	4.2
N-Methylformamide	30.1 [b)]	17.4 [b)]	18.8 [b)]	15.9 [b)]	423	538.0	1.7	5.9
Water	47.9	15.5	16.0	42.4	440	560.0	0.2	2.8

[a)] in units of [$mPa^{0.5}$] from J. E. Mark, ed., *Physical Properties of Polymers Handbook*, American Institute of Physics, Woodbury, N.Y., 1996;
[b)] from C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook, Second Edition*, CRC Press, Boca Raton, FL, 2007.

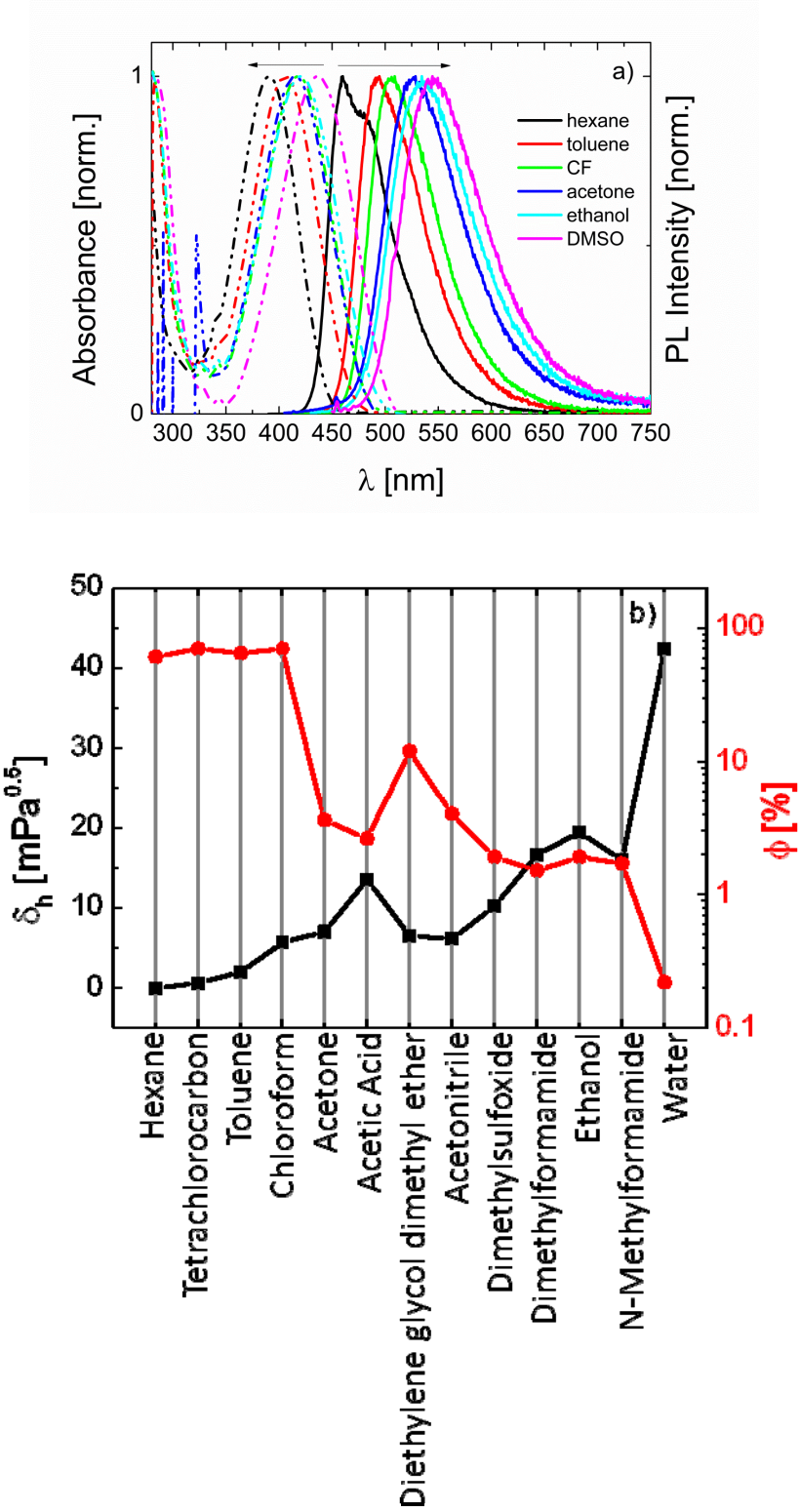


Fig. S3. a) The normalized absorbance and the photoluminescence spectra of the monomer (**3**) in selected solvents **b)** The relationship between the quantum yield (φ) of the monomer in various solvents and the corresponding hydrogen-bonding parameter (δ_h). All values are taken from Table S1.

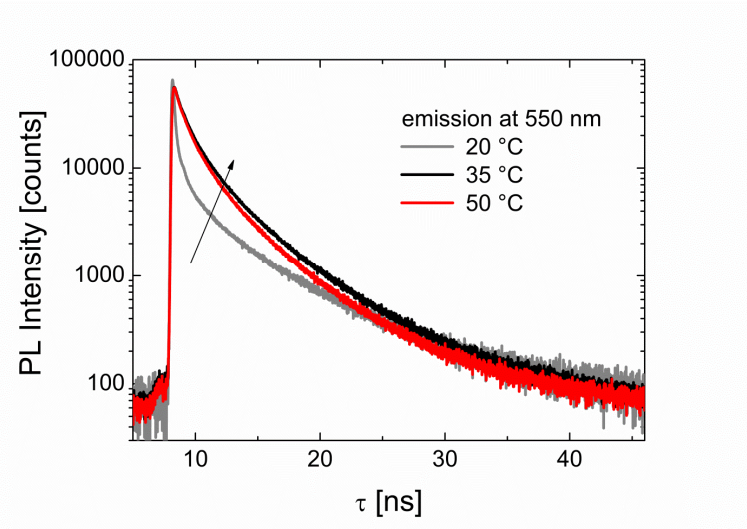


Fig. S4. Time-resolved PL traces of an aqueous solution of **P-1** at 20, 35, and 50 °C. The sample is excited at 470 nm and its emission is detected at 550 nm.

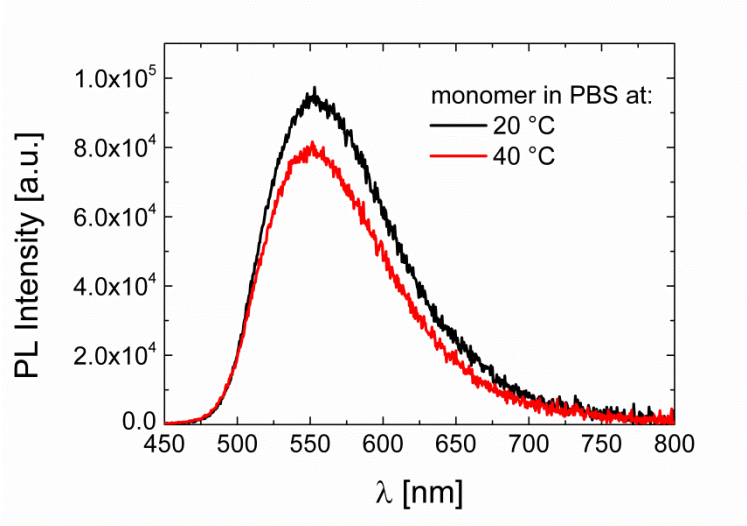


Fig. S5. Emission spectra of the 4-DMN labeled monomer in PBS at 20 and 40 °C.

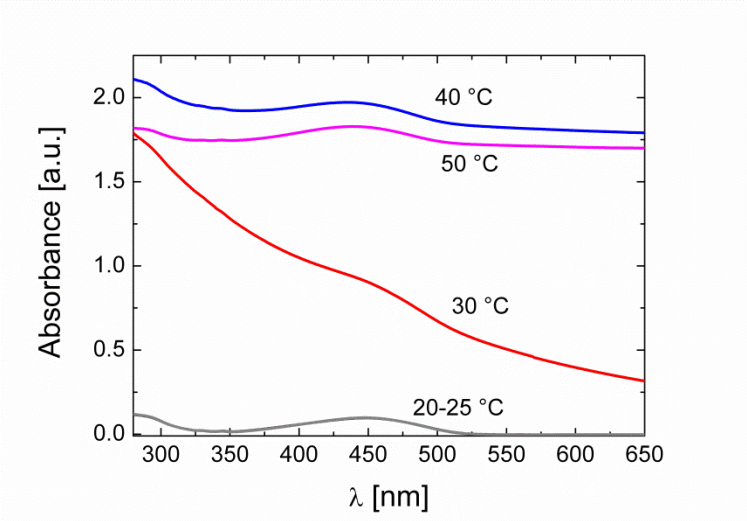


Fig. S6. Absorbance spectra of aqueous solution (0.5 g/L) of **P-1** measured in a 10 mm thick cuvette at various temperatures.

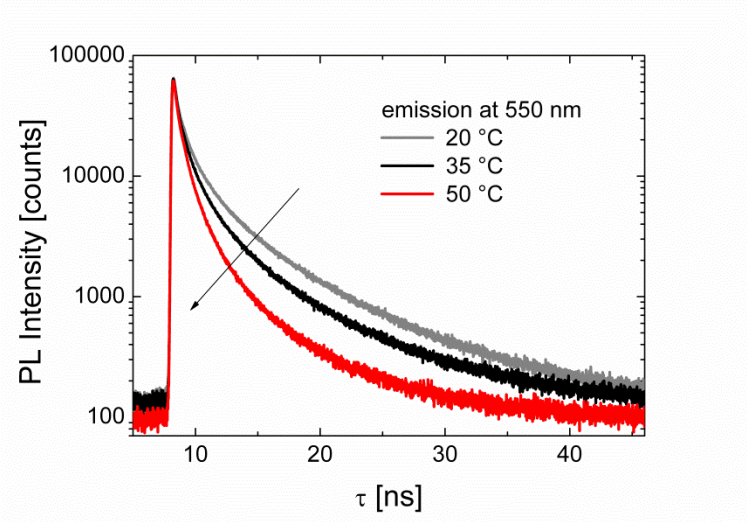


Fig. S7. Time-resolved PL traces of **P-3** aqueous solution at 20, 35, and 50 °C. The sample is excited at 470 nm and the emission is detected at 550 nm.

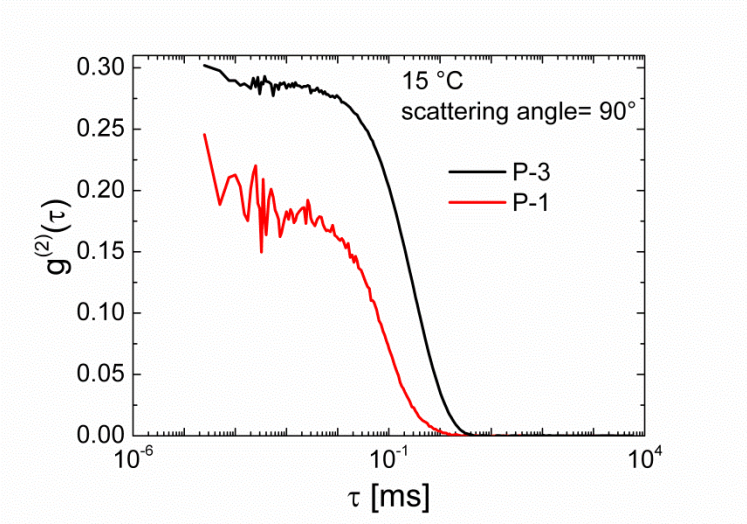


Fig. S8. The intensity-time autocorrelation functions of **P-1** (pNIPAm) and **P-3** (p(MEO_2MA-co-OEGMA)) solutions in PBS (0.1 g/L) at 15 °C recorded at a scattering angle of 90°, both showing a monomodal decay. For **P-1**, the noise is due to the very low scattering intensity of 5.5 10^{-6} cm^{-1}.