Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information: Understanding the Monomer Deuteration Effect on the Transition Temperature of poly(*N*-isopropylacrylamide) Microgels in H_2O

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Contents

1 Dynamic Light Scattering and Experimental Analysis

The sigmoid function, similar to [1], is given by

$$y = A_1 + (A_2 - A_1)\left(\frac{p}{1 + 10^{\left(\log(x_{01}) - x\right) h_1}} + \frac{1-p}{1 + 10^{\left(\log(x_{02}) - x\right) h_2}}\right) \quad (1)$$

and is fitted against the measurements of the NIPAM- and D_7NIPAM-based microgels as it is shown in Figure S1. Furthermore, the derivative of the sigmoid function is taken to calculate the VPTT shift. As a result, the VPTT shifts by 4.3 K.

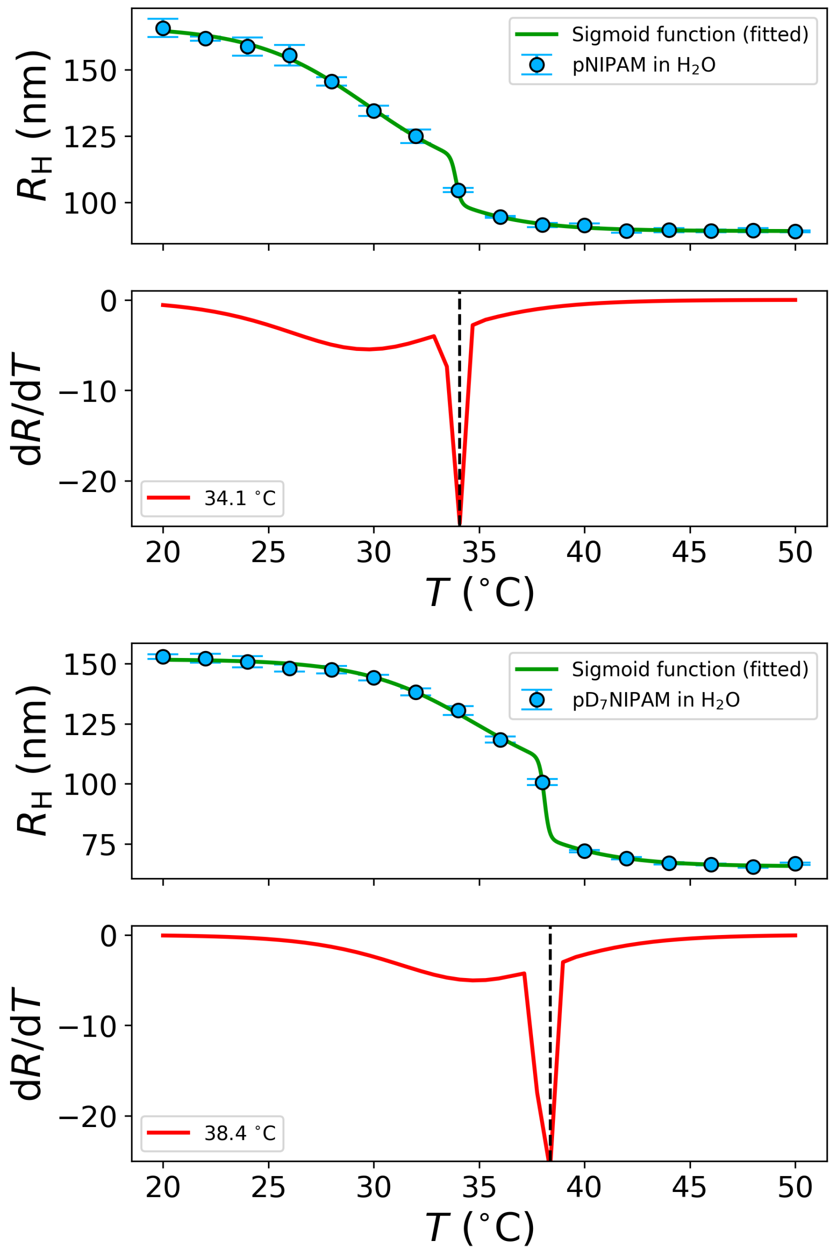

Figure S1 Experimental hydrodynamic radius R_H against temperature T for pNIPAM (top) and pD_7NIPAM (bottom) microgels in H_2O, respectively. A sigmoid function is fitted against both experimental measurements and its derivative is taken, resulting to a VPTT shift by 4.3 K.

The sigmoid function is fitted against the measurements of the ULC and pD_3NIPAM microgels in H_2O, and pNIPAM microgels in D_2O as it is shown in Figure S2, S3, and S4, respectively.

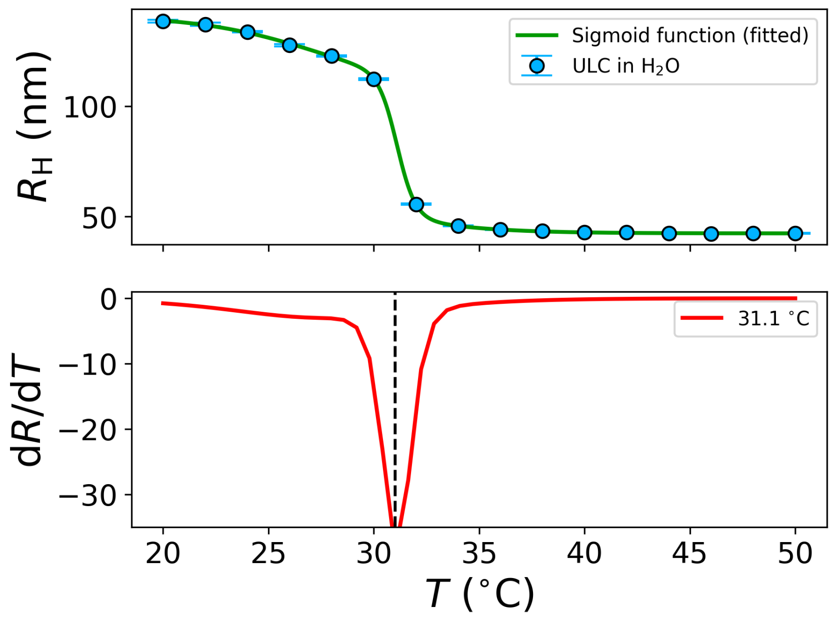

Figure S2 Experimental hydrodynamic radius R_H against temperature T for ULC microgels in H_2O. A sigmoid function is fitted against both experimental measurements and its derivative is taken, resulting to a VPTT of $31.1°C$.

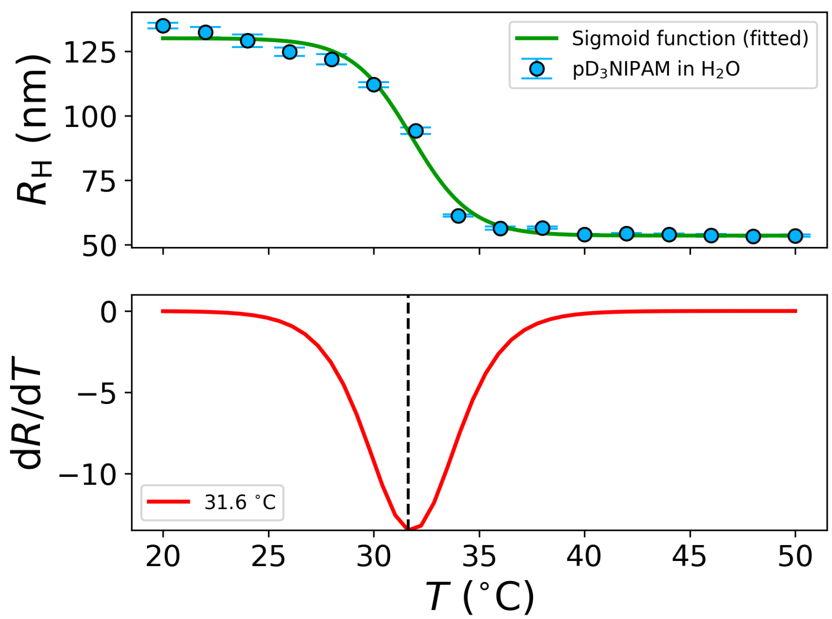

Figure S3 Experimental hydrodynamic radius R_H against temperature T for pD_3NIPAM microgels in H_2O. A sigmoid function is fitted against both experimental measurements and its derivative is taken, resulting to a VPTT of $31.6°C$.

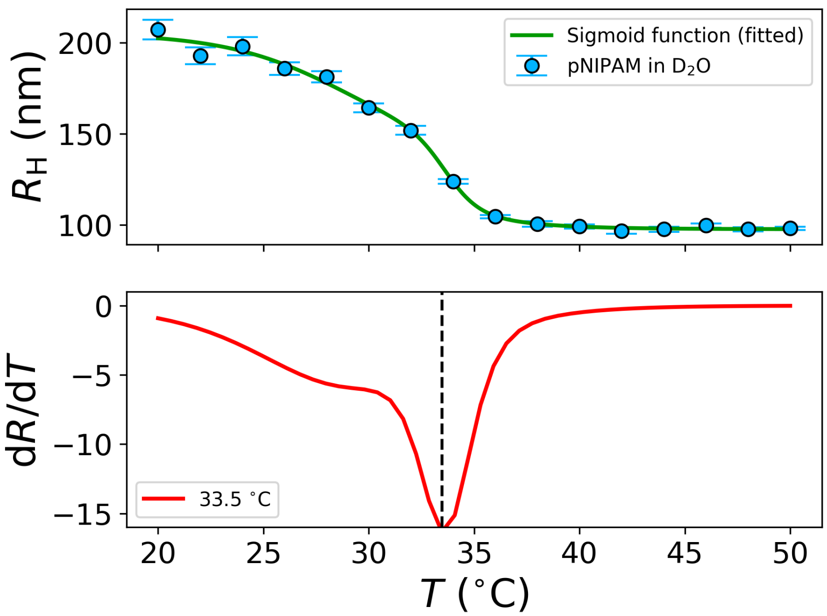

Figure S4 Experimental hydrodynamic radius R_{H} against temperature T for pNIPAM microgels in D_2O. A sigmoid function is fitted against both experimental measurements and its derivative is taken, resulting to a VPTT of $33.5°C$.

2 Estimation of ϕ_0 from measurements

The volume polymer fraction at the microgel preperation conditions is approximated by

$$\phi_0 = \frac{q}{k} \, , \tag{2}$$

where $k = 11.2$ is the conversion constant from viscosimetry and q is the swelling ratio is given by

$$q = \frac{R_h(20^o C)}{R_h(50^o C)} \, . \tag{3}$$

Using the above equations and error propagation analysis, we find $\phi_0 = 0.58 \pm 0.06$ and $\phi_0 = 0.51 \pm 0.03$ for the pNIPAM and pD$_7$NIPAM microgels, respectively.

3 Coefficient of determination

If y_i, $\bar{y}$, and f_i are the experimental data, the mean of the experimental data, and the calculated data, respectively, then the coefficient of determination is defined as,

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \tag{4}$$

where the residual sum of squares SS_{res} is defined as,

$$SS_{res} = \sum_i (y_i - f_i)^2 \tag{5}$$

and the total sum of squares SS_{res} is defined as,

$$SS_{res} = \sum_i (y_i - \bar{y})^2 \tag{6}$$

4 Derivation of $\Delta\chi_{\mathrm{qc}}$ from NIPAM- to D_7NIPAM-based microgels in H_2O

For simplification, we drop the subscript qc in the following derivation. The change in Flory-Huggins parameter from NIPAM- to D_7NIPAM-based microgels in H_2O is defined as,

$$\Delta\chi^{\mathrm{H_2O}}_{\mathrm{NIPAM,D_7NIPAM}} = \chi^{\mathrm{D_7NIPAM-H_2O}} - \chi^{\mathrm{NIPAM-H_2O}} \,. \tag{7}$$

To calculate the Flory-Huggins parameters in above equation, we consider the following reactions:

$$\frac{1}{2}\mathrm{C_6H_{11}NO{-}C_6H_{11}NO} + \frac{1}{2}\,(\mathrm{H_2O})_{2n} \rightleftharpoons \mathrm{C_6H_{11}NO{-}(H_2O)_n}$$

$$\frac{1}{2}\mathrm{C_6H_4D_7NO{-}C_6H_4D_7NO} + \frac{1}{2}\,(\mathrm{H_2O})_{2n} \rightleftharpoons \mathrm{C_6H_4D_7NO{-}(H_2O)_n}$$

where the $C_6H_{11}NO$ and $C_6H_4D_7NO$ refer to NIPAM and D_7NIPAM, respectively.
The Flory-Huggins parameters $\chi^{\mathrm{NIPAM-H_2O}}$ and $\chi^{\mathrm{D_7NIPAM-H_2O}}$ are defined as,

$$\chi^{\mathrm{NIPAM-H_2O}} = \frac{\Delta G_{\mathrm{NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{NIPAM-NIPAM}} + \Delta G_{\mathrm{(H_2O)_{2n}}}\right)}{RT} \tag{8}$$

and

$$\chi^{\mathrm{D_7NIPAM-H_2O}} = \frac{\Delta G_{\mathrm{D_7NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{D_7NIPAM-D_7NIPAM}} + \Delta G_{\mathrm{(H_2O)_{2n}}}\right)}{RT} \,. \tag{9}$$

Finally, combining the equations (7), (9), and (9), the change in Flory-Huggins parameter from NIPAM-based to D_7NIPAM-based microgels in H_2O is given by

$$\Delta\chi^{\mathrm{H_2O}}_{\mathrm{NIPAM,D_7NIPAM}} = \frac{\Delta G_{\mathrm{D_7NIPAM-(H_2O)_n}} - \Delta G_{\mathrm{NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{D_7NIPAM-D_7NIPAM}} - \Delta G_{\mathrm{NIPAM-NIPAM}}\right)}{RT} \,. \tag{10}$$

We note that we use only the zero-point energies to calculate the $\Delta\chi^{\mathrm{H_2O}}_{\mathrm{NIPAM,D_7NIPAM}}$, since all other contributions cancel exactly.

5 Derivation of $\Delta\chi_{\mathrm{qc}}$ for NIPAM-based microgels from H_2O to D_2O

For simplification, we drop the subscript qc in the following derivation. We note that for the pNIPAM microgels in D_2O, the hydrogen of the nitrogen exchanges with the solvent; therefore, this position gets deuterated. We consider the following reactions

$$\frac{1}{2}\mathrm{C_6H_{11}NO{-}C_6H_{11}NO} + \frac{1}{2}\,\mathrm{(H_2O)_{2n}} \rightleftharpoons \mathrm{C_6H_{11}NO{-}(H_2O)_n}$$

$$\frac{1}{2}\mathrm{C_6H_{10}DNO{-}C_6H_{10}DNO} + \frac{1}{2}\,\mathrm{(D_2O)_{2n}} \rightleftharpoons \mathrm{C_6H_{10}DNO{-}(D_2O)_n}\ ,$$

where the $C_6H_{11}NO$ and $C_6H_{10}DNO$ refer to NIPAM and D_1NIPAM when the nitrogen is with hydrogen and deuterium, respectively. To define the change in Flory-Huggins parameter for NIPAM-based microgels from H_2O to D_2O, we consider two steps: the change from NIPAM to D_1NIPAM in H_2O and of D_1NIPAM from H_2O to D_2O. We note that this is equivalent to the steps: the change of NIPAM from H_2O to D_2O and from NIPAM to D_1NIPAM in D_2O. Finally, the change in Flory-Huggins parameter for NIPAM-based microgels from H_2O to D_2O is defined as,

$$\Delta\chi^{\mathrm{NIPAM}}_{\mathrm{H_2O,D_2O}} = \frac{\Delta\chi^{\mathrm{H_2O}}_{\mathrm{NIPAM,D_1NIPAM}} + \Delta\chi^{\mathrm{D_1NIPAM}}_{\mathrm{H_2O,D_2O}}}{RT} = \frac{(\chi^{\mathrm{D_1NIPAM-H_2O}} - \chi^{\mathrm{NIPAM-H_2O}}) + (\chi^{\mathrm{D_1NIPAM-D_2O}} - \chi^{\mathrm{D_1NIPAM-H_2O}})}{RT}, \tag{11}$$

The Flory-Huggins interaction parameters $\chi^{\mathrm{NIPAM-H_2O}}$ and $\chi^{\mathrm{D_1NIPAM-H_2O}}$ are defined as,

$$\chi^{\mathrm{NIPAM-H_2O}} = \frac{\Delta G_{\mathrm{NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{NIPAM-NIPAM}} + \Delta G_{\mathrm{(H_2O)_{2n}}}\right)}{RT} \tag{12}$$

and

$$\chi^{\mathrm{D_1NIPAM-H_2O}} = \frac{\Delta G_{\mathrm{D_1NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{D_1NIPAM-D_1NIPAM}} + \Delta G_{\mathrm{(H_2O)_{2n}}}\right)}{RT}. \tag{13}$$

The change in Flory-Huggins interaction parameter from NIPAM to D_1NIPAM in H_2O is given by

$$\Delta\chi^{\mathrm{H_2O}}_{\mathrm{NIPAM,D_1NIPAM}} = \frac{\Delta G_{\mathrm{D_1NIPAM-(H_2O)_n}} - \Delta G_{\mathrm{NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{D_1NIPAM-D_1NIPAM}} - \Delta G_{\mathrm{NIPAM-NIPAM}}\right)}{RT}. \tag{14}$$

Analogously, the change in Flory-Huggins interaction parameter for D_1NIPAM from H_2O to D_2O is given by

$$\Delta\chi^{D_1NIPAM}_{H_2O,D_2O} = \frac{\Delta G_{D_1NIPAM-(D_2O)_n} - \Delta G_{D_1NIPAM-(H_2O)_n} - \frac{1}{2}\left(\Delta G_{\mathrm{(D_2O)_{2n}}} - \Delta G_{\mathrm{(H_2O)_{2n}}}\right)}{RT}. \tag{15}$$

Finally, combining the equations (14) and (15), the change in Flory-Huggins interaction parameter for NIPAM from H_2O to D_2O is given by

$$\Delta\chi^{\mathrm{NIPAM}}_{\mathrm{H_2O,D_2O}} = \frac{\Delta G_{\mathrm{D_1NIPAM-(D_2O)_n}} - \Delta G_{\mathrm{NIPAM-(H_2O)_n}} - \frac{1}{2}\left(\Delta G_{\mathrm{(D_2O)_{2n}}} - \Delta G_{\mathrm{(H_2O)_{2n}}} + \Delta G_{\mathrm{D_1NIPAM-D_1NIPAM}} - \Delta G_{\mathrm{NIPAM-NIPAM}}\right)}{RT}. \tag{16}$$

A complex of $(H_2O)_{2n}$ molecules for the ΔG_{SS} is required to have the correct stoichiometry. For pD_7NIPAM microgels in H_2O, we note this is irrelevant as this term cancels out. We study the effect of one D_2O molecule to $\Delta\chi_{\mathrm{qc}}$. We find that $\Delta\chi_{\mathrm{qc}}$ takes the values -0.01 (RT) and 0.12 (RT) when the D_2O creates a hydrogen bond with the CO and NH group, respectively. To increase the accuracy of $\Delta\chi_{\mathrm{qc}}$, one expects that more D_2O molecules are required to solvate NIPAM (similar to what we find in the pD_7NIPAM microgels in H_2O). However, this is not as trivial as in the case of pD_7NIPAM microgels in H_2O; one realizes that the terms $(H_2O)_n$ and $\frac{1}{2}(H_2O)_{2n}$ do not have the same number of hydrogen bonds in both sides of the reaction influencing the $\Delta\chi_{\mathrm{qc}}$ value. Despite our efforts, our approach has yet to be applicable to the pNIPAM microgels in the D_2O system. A detailed study is required to find a way to deuterate the NIPAM and avoid the effects mentioned above.

6 Zero-point energies

Table S1 Zero-point energies of the molecular structures under study.

Molecular structures	ZPE (Hartree)
NIPAM-NIPAM	0.329456
D_7NIPAM-D_7NIPAM	0.283613
NIPAM-1H_2O	0.188111
NIPAM-2H_2O	0.21291
NIPAM-3H_2O	0.238955
NIPAM-4H_2O	0.265725
NIPAM-5H_2O	0.291532
NIPAM-6H_2O	0.317277
NIPAM-7H_2O	0.34432
NIPAM-8H_2O	0.370073
NIPAM-9H_2O	0.394123
NIPAM-10H_2O	0.422221
NIPAM-14H_2O	0.522915
NIPAM-25H_2O	0.807
NIPAM-27H_2O	0.857955
NIPAM-40H_2O	1.194076
D_7NIPAM-1H_2O	0.165186
D_7NIPAM-2H_2O	0.189985
D_7NIPAM-3H_2O	0.21601
D_7NIPAM-4H_2O	0.24276
D_7NIPAM-5H_2O	0.268569
D_7NIPAM-6H_2O	0.294275
D_7NIPAM-7H_2O	0.321352
D_7NIPAM-8H_2O	0.347109
D_7NIPAM-9H_2O	0.371173
D_7NIPAM-10H_2O	0.399205
D_7NIPAM-14H_2O	0.499785
D_7NIPAM-25H_2O	0.783607
D_7NIPAM-27H_2O	0.83455
D_7NIPAM-40H_2O	1.170671
1H_2O	0.021178
2H_2O	0.045881
3H_2O	0.072951
4H_2O	0.098698
5H_2O	0.124291
6H_2O	0.151048
7H_2O	0.176655
8H_2O	0.204093
9H_2O	0.228877
10H_2O	0.255152
14H_2O	0.356023
25H_2O	0.640694
27H_2O	0.692056
40H_2O	1.029922
2D_2O	0.033493
D_1NIPAM-1D_2O	0.177885
D_1NIPAM-D_1NIPAM	0.32143
NIPAM-1H_2O (hydrogen bond with N)	0.187161
D_1NIPAM-1D_2O (hydrogen bond with N)	0.177152

References

[1] M. Cors, L. Wiehemeier, J. Oberdisse and T. Hellweg, *Polymers*, 2019, **11**,.