Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

On the Molecular Origin of the Cooperative Coil-to-globule Transition of Poly(N-isopropylacrylamide) in Water

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Table S1. Stereochemistry and initial backbone conformation of PNIPAM 30-mer.

Residue number	Configuration	Conformation
1	*l*	tt
2	*d*	tt
3	*l*	tt
4	*d*	g*t
5	*d*	g*t
6	*d*	g*t
7	*l*	gt
8	*l*	gt
9	*d*	tt
10	*l*	tt
11	*d*	tt
12	*l*	gt
13	*l*	gt
14	*l*	gt
15	*d*	tt
16	*l*	gt
17	*l*	gt
18	*l*	gt
19	*l*	gt
20	*l*	gt
21	*d*	g*t
22	*d*	g*t
23	*d*	g*t
24	*l*	gt
25	*l*	gt
26	*d*	g*t
27	*d*	g*t
28	*l*	tt
29	*d*	tt
30	*l*	-

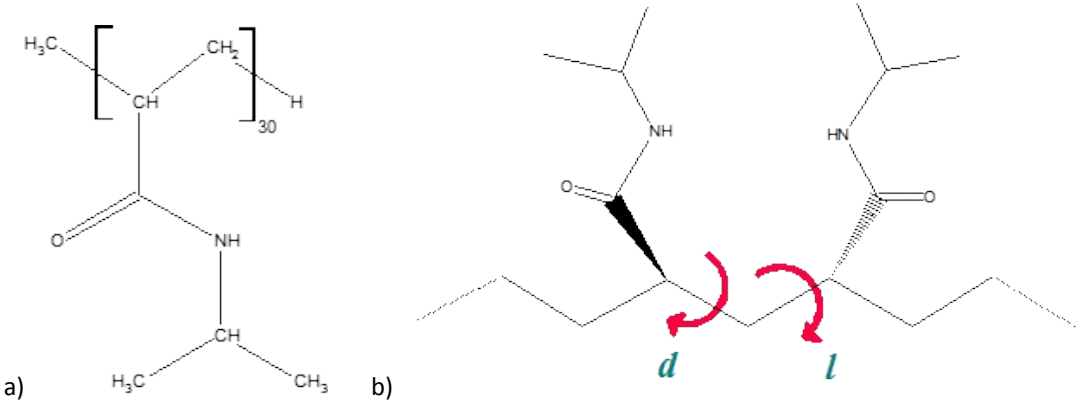

Fig. S1 Illustration of the chemical structure of the PNIPAM 30-mer (a) and definition of the residues configuration (b). Arrows indicate dihedral backbones.

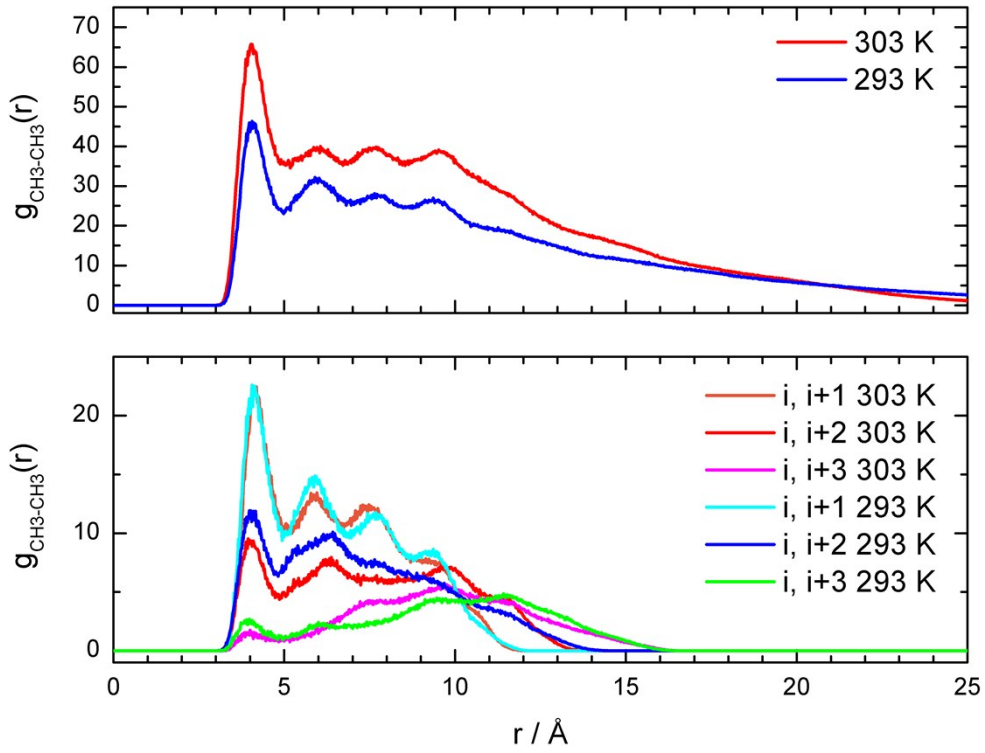

Fig. S2 Pair distribution functions of PNIPAM methyl groups as calculated from the MD simulations. On the upper panel the total distributions at 303 K and 293 K are shown in blue and red, respectively. On the lower panel the contributions of the i, i+1 residues (orange at 303 K and light blue at 293 K), i, i+2 residues, (red at 303 K and blue at 293 K) and i, i+3 residues (magenta at 303 K and green at 293 K) are represented individually.

The clustering of methyl groups at 303 K, visible by comparing the radial distribution functions between methyl carbon atoms, rdf_{CC}, at 293 and 303 K (Fig. S2 of ESI), confirms that the backbone conformational transition observed at 303 K is concerted with a rearrangement of side chain groups to minimize the exposed hydrophobic surface area. Ahmed at al. proposed that the hydrophobic collapsed state may be formed by pushing the i, i + 3 isopropyl groups closer together to form local hydrophobic pockets.[S1] We selectively analysed the rdf_{CC} between pair of PNIPAM residues and found no increment of clustering between i, i + 3 isopropyl groups at 303 K.

Table S2. Average time of transitions of the backbone dihedrals $<\tau_b>$ and the dihedrals of the methyl groups $<\tau_m>$ as function of the temperature.

Temperature (K)	$<\tau_b>$ (ns)	$<\tau_m>$ (ps)
243	-*	340±20
253	-*	270±10
263	70±20	200±10
273	40±10	150±4
283	20±10	130±4
293	10±2	110±2
303	10±5	90±2
313	5±1	74±2
323	5±1	60±0.3

**Average time of transition not defined due to reduced sampling.*

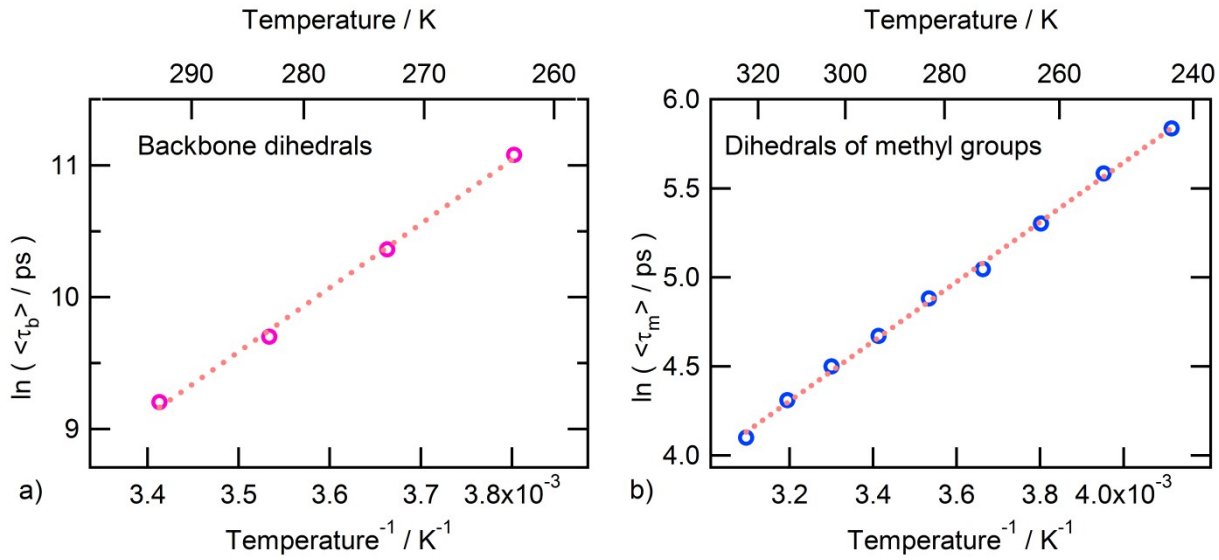

Fig. S3 Arrhenius plot of the average lifetime of a rotational state of a backbone dihedral (a) and of a dihedral of a methyl group (b). Dashed line shows the linear fit of the data.

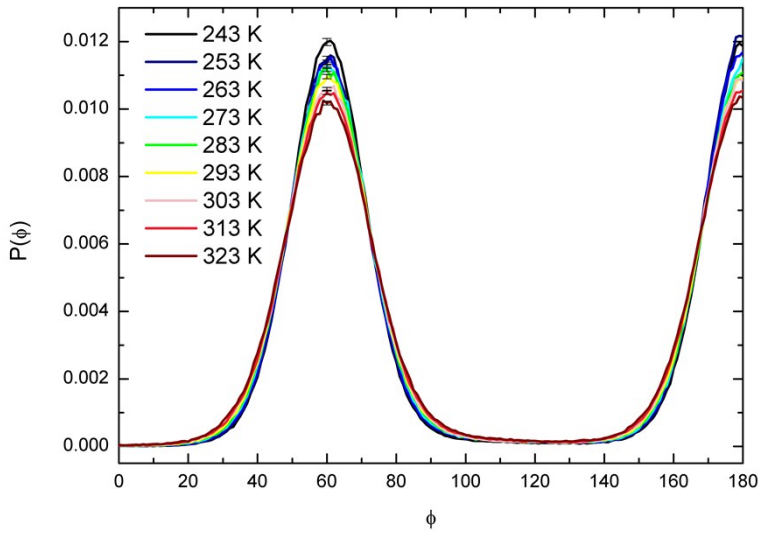

Fig. S4 Distribution of dihedral angles of PNIPAM methyl groups as a function of the temperature.

Table S3. Average number of hydration water molecules per PNIPAM residue.

Temperature (K)	Hydration water molecules *per* residue
243	14.3±0.3
253	14.5±0.3
263	13.9±0.3
273	14.0±0.4
283	14.2±0.4
293	13.7±0.5
303	11.5±0.5
313	12.2±0.6
323	11.4±0.6

**Time averaged values and standard deviation.*

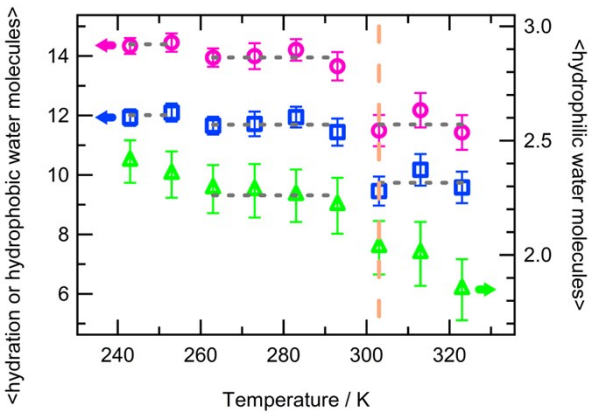

Fig. S5 Temperature dependence of the average number of FHS water molecules *per* residue classified as total hydration water molecules (pink circles), hydrophobic water molecules (blue squares) and hydrophilic water molecules (green triangles). Data represent time averaged values and standard deviation. Dashed lines are guide to the eye.

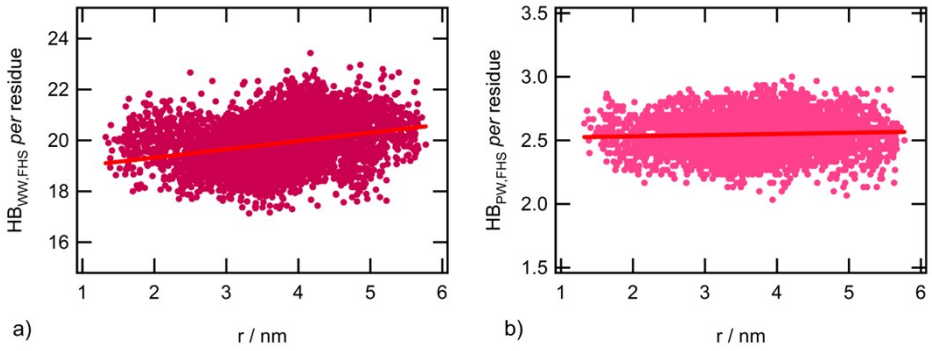

Fig. S6 a) Correlation between hydrogen bonding of water molecules *per* repeating unit in the FHS and end to end distance (r), for PNIPAM 30-mer at 293 K. b) Correlation between PNIPAM-water hydrogen bonding and end to end distance, for PNIPAM 30-mer at 293 K.

Table S4. Comparison between hydrogen bonding of bulk water and of water hydrating PNIPAM hydrophobic groups.*

Temperature (K)	293	303	313
Number of HBs (*per* water molecule) in bulk water	2.18 ± 0.01	2.20 ± 0.01	2.20 ± 0.01
Number of HBs (*per* water molecule) in the first hydration shell of PNIPAM isopropyl groups	1.42 ± 0.03	1.40 ± 0.03	1.40 ± 0.03

*Errors are estimated by standard deviation.

Supplementary movie

Time evolution of PNIPAM chain conformation and its first hydration shell at 283 K (on the left) and 303 K (on the right) over the first 150 ns of simulation. PNIPAM backbone atoms are shown in white, hydrophilic water oxygen atoms in red and hydrophobic water oxygen atoms in blue.

References

S1 Z. Ahmed, E. A. Gooding, K. V. Pimenov, L. Wang and S. A. Asher, *The Journal of Physical Chemistry* B, 2009, **113**, 4248-4256.