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

Solution behaviour of poly(N-isopropylacrylamide) stereoisomers: a molecular dynamics simulation study

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Electronic Supplementary Information

Contents

1. Interchain Radial Distribution Functions

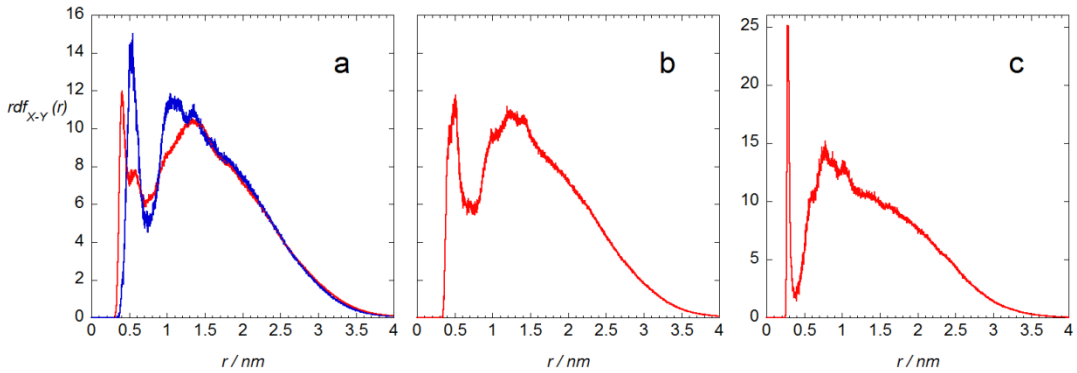

Figure 1. Radial distribution functions between atoms belonging to different PNIPAM chains, calculated for m45_2 at 323 K in a time interval of 30 ns within the production run. **(a)** CE_CF(A) – CE_CF(B) and CI(A) – CI(B), red and blue curve, respectively. **(b)** CE_CF(A) – CI(B). **(c)** N(A) – OC(B).
The letters A and B indicate the chain, CE and CF are the carbon atoms of the methyl groups of the isopropyl moiety and CI is the tertiary carbon atom of the isopropyl moiety. N and OC are nitrogen and oxygen atom of the amide group.

2. Polymer-Polymer Hydrogen Bonding

Table 1. Features of Polymer-Polymer Hydrogen Bonding

Temperature (K)	System	Chain	Number of HB's *per* residue[a]	Fraction of HB's between selected pairs of residues					
				n-(n+1)[b]	n-(n+2)[c]	n-(n+3)[d]	n-(n+4)[e]	n-(n+5)[f]	n-(n+k)[g] k>5
283	m45_2	A	0.07(1)	0.54	0.39	0.00	0.06	0.00	0.01
		B	0.07(1)	0.51	0.41	0.00	0	0	0.08
	m59_2	A	0.09(1)	0.71	0.19	0.05	0.01	0	0.04
		B	0.06(1)	0.34	0.63	0.00	0	0	0.03
323	m45_2	A	0.12(2)	0.64	0.29	0.01	0	0.02	0.04
		B	0.12(2)	0.41	0.42	0.08	0.08	0.00	0.00
	m59_2	A	0.14(2)	0.69	0.12	0.03	0.15	0	0.01
		B	0.14(2)	0.50	0.36	0.03	0.02	0	0.09

[a]. Time average and standard deviation over the production run.

[b]. Fraction of HB's formed between adjacent residues.

[c]. Fraction of HB's formed between residues separated by 1 repeating unit.

[d]. Fraction of HB's formed between residues separated by 2 repeating units.

[e]. Fraction of HB's formed between residues separated by 3 repeating units.

[f]. Fraction of HB's formed between residues separated by 4 repeating units.

[g]. Fraction of HB's formed between residues separated by more than 4 repeating units.

4. Coil-Globule Transition of Single Chains above the LCST

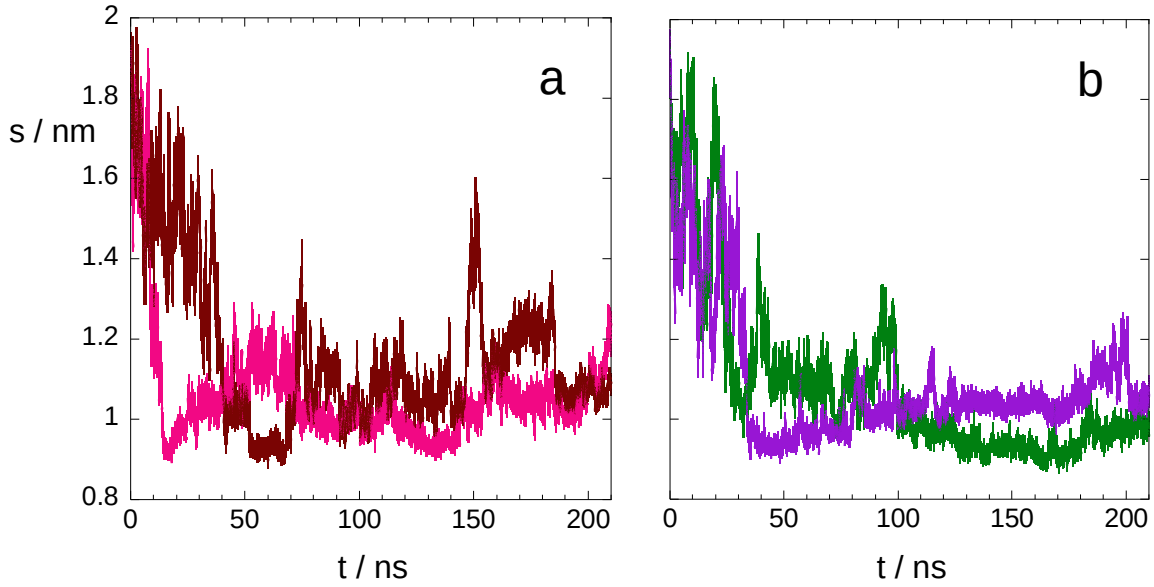

Figure 2. (a) Time behaviour of the radius of gyration of A and B chains (purple and brown curves, respectively) of m45_2 at 323 K. (b) Time behaviour of the radius of gyration of A and B chains (green and violet curves, respectively) of m59_2 at 323 K.

4. Time Evolution of Inter-residue Contacts

The matrix of the mean smallest distances between atoms of pairs of residues was calculated with a time average of 2 ns along the whole trajectory. Residues numbered from 1 to 30 form the first 30-mer, residues numbered from 31 to 60 form the second 30-mer. The 105 images of the map were collected in a movie, displaying the time behaviour of both intra and interchain contacts between residues. The residues located within isotactic sequences were labelled with a dot on the diagonal of the matrix, at the aim to highlight a preferential connectivity of such chain regions. The label PR in the movie indicates the time interval of production run.

Below the LCST:

files movie_m45_2_283K.avi, movie_m59_2_283K.avi

Above the LCST:

files movie_m45_2_323K.avi, movie_m59_2_323K.avi.