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

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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

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>System</th>
<th>Chain</th>
<th>Number of HB’s per residue</th>
<th>Fraction of HB’s between selected pairs of residues</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n-(n+1)</td>
</tr>
<tr>
<td>283</td>
<td>m45_2</td>
<td>A</td>
<td>0.07(1)</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>0.07(1)</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>m59_2</td>
<td>A</td>
<td>0.09(1)</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>0.06(1)</td>
<td>0.34</td>
</tr>
<tr>
<td>323</td>
<td>m45_2</td>
<td>A</td>
<td>0.12(2)</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>0.12(2)</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>m59_2</td>
<td>A</td>
<td>0.14(2)</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>0.14(2)</td>
<td>0.50</td>
</tr>
</tbody>
</table>

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.