Supplementary Document

Atomistic Molecular Dynamics Simulations of The Lower Critical Solution Temperature Transition of Poly(N-vinylcaprolactam) in Aqueous Solutions

Xiaoquan Sun and Xianghong Qian*

Department of Biomedical Engineering, University of Arkansas, Fayetteville, AR 72701

The force field parameters for the MD simulations of PVCL polymer in water and in salt solutions were determined from quantum mechanical calculations. Table S1 lists the charges on the atoms according to the naming and numbering of three fragments, the head, the middle and the tail regions as shown in Figure S1.

Table S1 RESP atomic charges of each fragment of PVCL

Head		Middle		End	
Atom	**Charges**	**Atom**	**Charges**	**Atom**	**Charges**
C1	0.025	C6	0.478	C6	0.490
C2	-0.029	N1	-0.461	H9	-0.050
H3	0.016	C5	0.608	C9	-0.144
H4	0.016	C3	-0.149	H12	0.074
C4	0.013	C1	0.024	C10	-0.256
H7	0.024	C2	-0.030	H14	0.060
H8	0.024	H3	0.015	H15	0.060
C8	-0.079	H4	0.015	H16	0.060
H10	0.064	C4	0.012	H13	0.074
H11	0.064	H7	0.023	N1	-0.451
H1	0.001	H8	0.023	C8	-0.080
H2	0.001	C8	-0.082	C4	0.013
C3	-0.143	H10	0.062	C2	-0.029
H5	0.068	H11	0.062	H3	0.015
H6	0.068	H1	0.001	H4	0.015
C5	0.638	H2	0.001	H7	0.023
O1	-0.658	H5	0.065	H8	0.023
N1	-0.445	H6	0.065	H10	0.063
C6	0.497	O1	-0.677	H11	0.063
H9	-0.049	H9	-0.051	C5	0.624
C7	-0.479	C9	-0.148	O1	-0.662
H17	0.119	H12	0.072	C3	-0.145
H18	0.119	H13	0.072	H5	0.067
H19	0.119			H6	0.067
C9	-0.142			C1	0.025
H12	0.075			H1	0.001
H13	0.075			H2	0.001

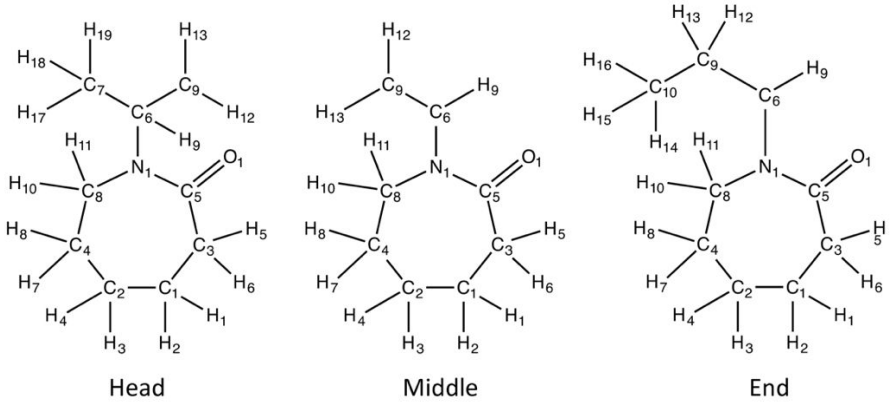

Figure S1 The naming and numbering of the fragments on PVCL chain.

The force field parameters of three bonds (C-CT, C-N, CT-N) were obtained by SCAN in Gaussian09 at the MP2/6-31G* level. PARAMFIT in AMBERTOOLS15 was applied for fitting the angles and dihedrals on the ring. Based on the various input conformations, PARAMFIT adjusted multiple force field parameters simultaneously and then compared the potential energies obtained from AMBER using the adjusted force field parameters with the ones calculated quantum mechanically using Gaussian09. Here 346 conformations were used during the fitting process. The atom type of monomer as shown in Figure S2 and the resulting force field parameters as shown in Table S2 were listed below.

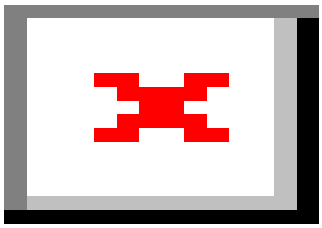

Figure S2 Atom type of the monomer

Table S2 The fitting force field parameters with AMBER format.

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BOND
C -CT  287.0    1.534
C -N   459.1    1.382
CT-N   317.7    1.478

ANGLE
CT-C -N    132.9      120.27
CT-CT-N     88.9      112.30
C -N -CT    97.9      126.92
N -C -O    137.4      121.52
H1-CT-N     68.0      109.88
CT-N -CT   103.4      113.40

DIHE
N -CT-CT-HC    1        -0.1418        73.6893         3.0000
H1-CT-N -CT    1        -1.1235       167.6092         2.0000
HC-CT-C -N     1        -6.1616       379.4880         2.0000
C -CT-CT-HC    1         1.7594        86.2718         3.0000
C -N -CT-H1    1         2.8172        35.2472         2.0000
O -C -CT-HC    1        -7.0339       159.2257        -1.0000
O -C -CT-HC    1        -8.2311       576.1304        -2.0000
O -C -CT-HC    1         0.3923      -102.0159         3.0000
CT-CT-CT-CT    1        -0.7627       107.8859        -1.0000
CT-CT-CT-CT    1         0.4300       149.3185        -2.0000
CT-CT-CT-CT    1         0.8874       179.4886         3.0000
N -CT-CT-CT    1         1.1856        -1.3348         3.0000
CT-N -CT-CT    1        -0.8330        36.4871         2.0000
CT-CT-C -N     1         3.2207       106.7447        -2.0000
CT-CT-C -N     1         1.6201       297.6333         4.0000
CT-C -N -CT    1         2.8185       226.5267         2.0000
C -CT-CT-CT    1         0.1775      -108.0146         3.0000
C -N -CT-CT    1         3.9234       -15.3719        -1.0000
C -N -CT-CT    1         2.2871        58.5465        -2.0000
C -N -CT-CT    1         1.3048        -2.7913        -3.0000
C -N -CT-CT    1         0.6132        41.5675         4.0000
O -C -CT-CT    1         1.1485       116.2575         2.0000
O -C -N -CT    1         3.2915       180.0004         2.0000

IMPR
C -CT-N -CT            -2.8185       171.2667         2.0000
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