Structural and dynamical properties of Polyethylenimine in explicit water at different protonation states: A Molecular Dynamics Study†

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Table S1 Coulombic parameters (q_i, see Equation 2) for unprotonated PEI chain. See Figure S1(a) for atom numbers.

Atom No.	Atom name	Atom type	Charge, q_i
1	N	amber99_38 (N2)	- 0.740
2, 3	H1, H2	amber99_17 (H)	0.250
4	CA	amber99_11 (CT)	- 0.140
5, 6, 8, 9	HA1, HA2, HB1, HB2	amber99_19 (H1)	0.115
7	CB	amber99_11 (CT)	-0.080
10	N	amber99_81 (NT)	-0.593
11,	H	amber99_17 (H)	0.269
12, 15	CA, CB	amber99_11 (CT)	- 0.086
13, 14, 16, 17	HA1, HA2, HB1, HB2	amber99_19 (H1)	0.124
18	N	amber99_81 (NT)	-0.500
19,	H	amber99_17 (H)	0.280
20	CA	amber99_11 (CT)	- 0.081
21, 22	HA1, HA2	amber99_19 (H1)	0.125
23	CB	amber99_11 (CT)	- 0.300
24, 25, 26	HB1, HB2, HB3	amber99_18 (HC)	0.117

Table S2 Coulombic parameters (q_i, see Equation 2) for alternate protonated PEI chain. See Figure S1(b) for atom numbers.

Atom No.	Atom name	Atom type	Charge, q_i
1	N	amber99_81 (NT)	- 0.417
2, 3, 4	H1, H2, H3	amber99_17 (H)	0.360
5	CA	amber99_11 (CT)	0.056
6, 7	HA1, HA2	amber99_19 (H1)	0.087
8	CB	amber99_11 (CT)	-0.147
9, 10	HB1, HB2	amber99_19 (H1)	0.127
11	N	amber99_81 (NT)	-0.593
12	H	amber99_17 (H)	0.269
13, 16	CA, CB	amber99_11 (CT)	- 0.086
14, 15, 17, 18	HA1, HA2, HB1, HB2	amber99_19 (H1)	0.124
19	N	amber99_81 (NT)	-0.150
20, 21	H1, H2	amber99_17 (H)	0.340
22, 25	CA , CB	amber99_11 (CT)	- 0.023
23, 24, 26, 27	HA1, HA2, HB1, HB2	amber99_19 (H1)	0.129
28	N	amber99_81 (NT)	-0.500
29	H	amber99_17 (H)	0.280
30	CA	amber99_11 (CT)	- 0.081
31, 32	HA1, HA2	amber99_19 (H1)	0.125
33	CB	amber99_11 (CT)	- 0.300
34, 35, 36	HB1, HB2, HB3	amber99_18 (HC)	0.117

Table S3 Coulombic parameters (q_i, see Equation 2) for completely protonated PEI chain. See Figure S1(c) for atom numbers.

Atom No.	Atom name	Atom type	Charge, q_i
1	N	amber99_81 (NT)	- 0.417
2, 3, 4	H1, H2, H3	amber99_17 (H)	0.36
5	CA	amber99_11 (CT)	0.056
6, 7	HA1, HA2	amber99_19 (H1)	0.087
8	CB	amber99_11 (CT)	-0.147
9, 10	HB1, HB2	amber99_19 (H1)	0.127
11	N	amber99_81 (NT)	-0.150
12, 13	H1, H2	amber99_17 (H)	0.340
14, 17	CA, CB	amber99_11 (CT)	- 0.023
15, 16, 18, 19	HA1, HA2, HB1, HB2	amber99_19 (H1)	0.129
20	N	amber99_81 (NT)	-0.135
21, 22	H1, H2	amber99_17 (H)	0.331
23	CA	amber99_11 (CT)	- 0.067
24, 25	HA1, HA2	amber99_19 (H1)	0.120
26	CB	amber99_11 (CT)	- 0.314
27, 28, 29	HB1, HB2, HB3	amber99_18 (HC)	0.160

Table S4 Lennard Jones parameters (σ and ε, see Equation 2) for the atom types mentioned in Table S1, Table S2, and Table S3.

Atom type	σ, nm	ε, kJ mol^{-1}
amber99_11 (CT)	0.339967	0.4577300
amber99_17 (H)	0.106908	0.0656888
amber99_18 (HC)	0.264953	0.0656888
amber99_19 (H1)	0.247135	0.0656888
amber99_38 (N2)	0.325000	0.7112800
amber99_81 (NT)	0.325000	0.7112800

Table S5 Bond parameters (b_0 and k_{ij}^{bonds}, see Equation 1) for the bond between the atom types (ij) in Table S1, Table S2 and Table S3.

Bond (Atom types, ij)	b_0, nm	k_{ij}^{bonds}, kJ mol^{-1} nm^2
H - N2	0.10100	363171.2
N2 - CT	0.14630	282001.6
CT - H1	0.10900	284512.0
CT - CT	0.15260	259408.0
CT - NT	0.14710	307105.6
NT - H	0.10100	363171.2
CT - HC	0.10900	284512.0

Table S6 Bonded angle parameters (θ_0 and k_{ijk}^{angle}) for angles formed by the atom types (ijk) mentioned in Table S1, Table S2 and Table S3.

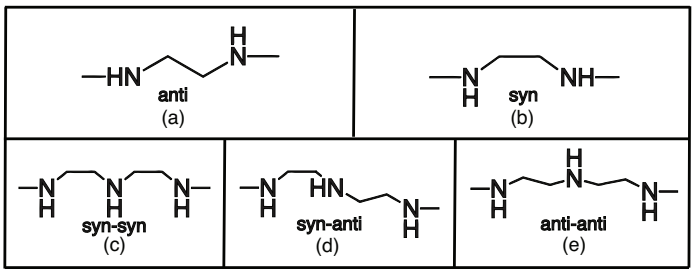
Angles (Atom types, ijk)	θ_0, °	k_{ijk}^{angle}, kJ mol^{-1} rad^2
H - N2 - H	120.0	292.880
H - N2 - CT	118.4	418.400
N2 - CT - H1	109.5	418.400
N2 - CT - CT	111.2	669.400
CT - CT - H1	109.5	418.400
H1 - CT - H1	109.5	292.800
CT - CT - NT	111.2	669.400
CT - NT - H	109.5	418.400
NT - CT - H1	109.5	418.400
CT - NT - CT	109.5	418.400
CT - CT - HC	109.5	418.400
HC - CT - HC	109.5	292.800
H - NT - H	109.5	292.880

Table S7 Dihedral parameters (ϕ_s and $k_{ijkl}^{dihedral}$, see Equation 1) for Harmonic functions and the values of C_n for Ryckaert-Bellemans functions. X denotes any undefined atom types in the harmonic functions in Table S1, Table S2 and Table S3

Dihedral (Atom types), $ijkl$	ϕ_s	$k_{ijkl}^{dihedral}$ (kJ mol^{-1})	n
H - N2 - CT - CT	0.0	3.7656	3
H - NT - CT - CT	0.0	3.7656	3
H - NT - CT - H1	0.0	3.7656	3
CT - CT - NT - CT	0.0	0.6276	3
CT - CT - NT - CT	180.0	1.004	2

Dihedral (Atom types), $ijkl$, kJ mol^{-1}	C_0	C_1	C_2	C_3	C_4	C_5
X - N2 - CT - X	0.0	0.0	0.0	0.0	0.0	0.0
X - CT - CT - X	0.65084	1.95253	0.0	-2.60338	0.0	0.0

Table S8 Possible nearest neighbor (a, b) and next nearest neighbour (c, d and e) conformations for the PEI chain



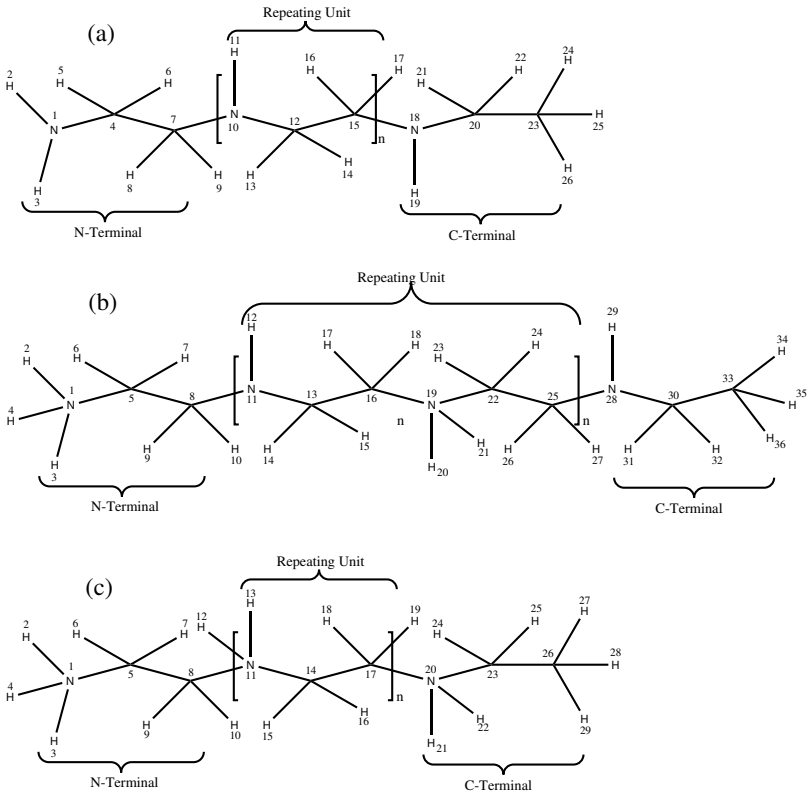


Fig. S1 Structure of PEI with atom number. (a) Unprotonated chain, (b) Alternate protonated, and (c) completely protonated chain. For unprotonated and completely protonated chain n = 18 for 20-mer and 48 for 50-mer, while for alternated protonated chain, n = 9 and 24 for 20 and 50-mer, respectively. The atoms are numbered for Table S1,Table S2 and Table S3.

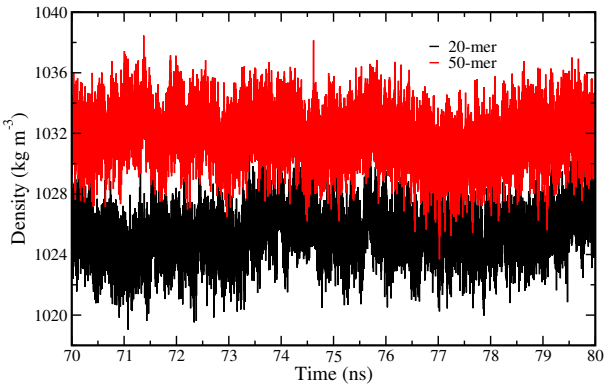


Fig. S2 The variation of density of 20 and 50-mer PEI with time.

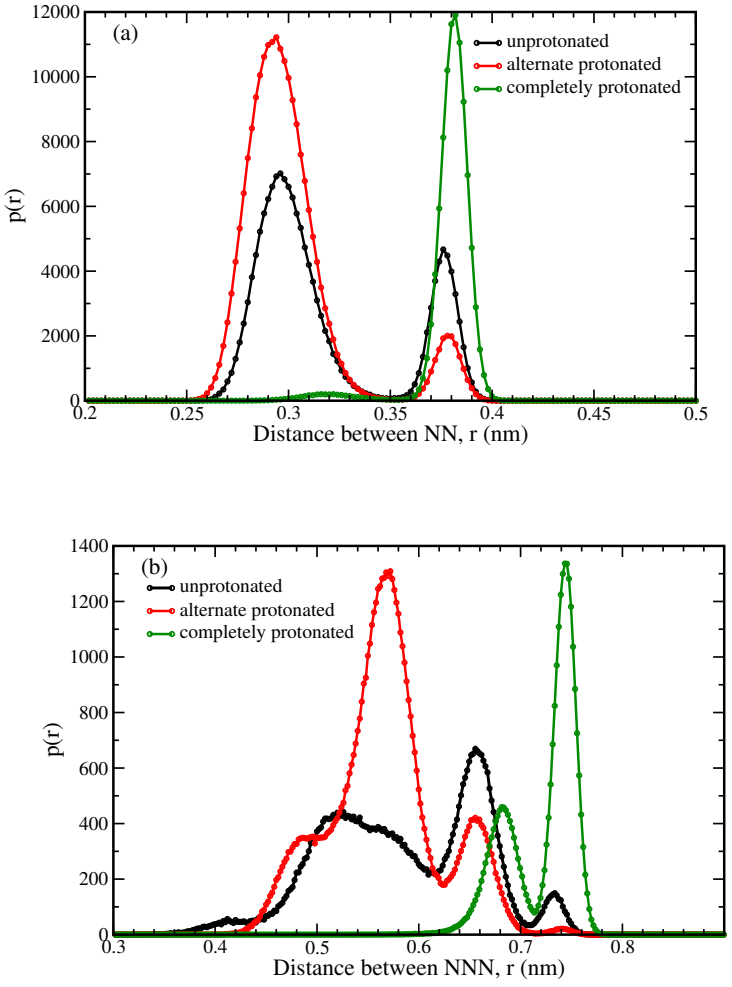


Fig. S3 (a) The nearest neighbour, NN and (b) The next nearest neighbour, NNN distributions of the nitrogen atoms for the 20-mer PEI.

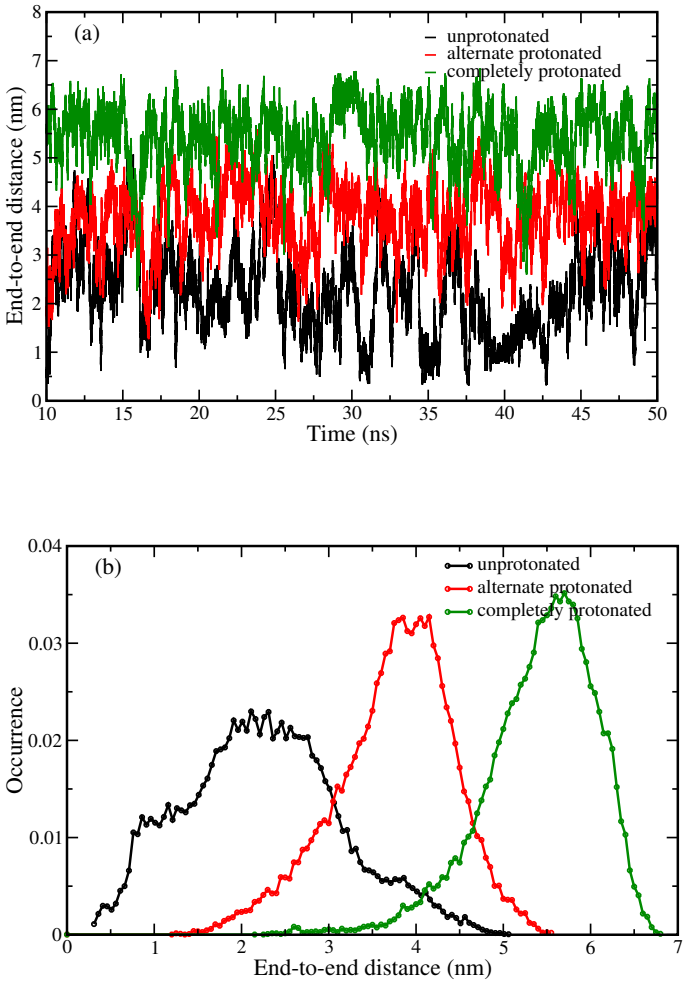


Fig. S4 (a) End-to-end distance and (b) its distribution of 20-mer PEI for different protonation states.

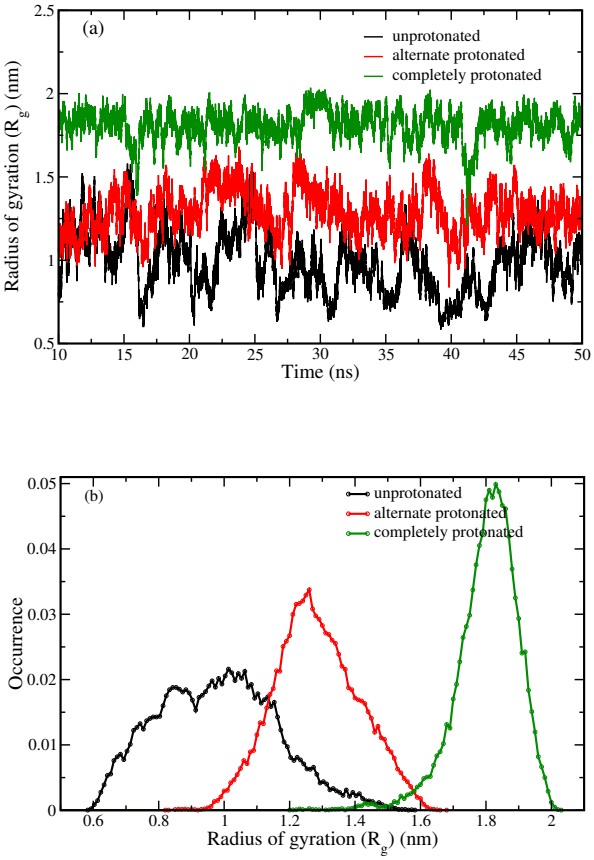


Fig. S5 (a) Radius of Gyration and (b) its distribution of 20-mer PEI for different protonation states.

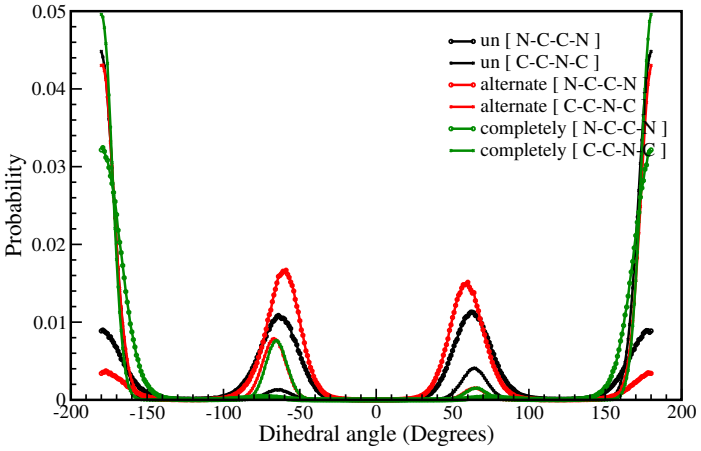


Fig. S6 Dihedral distribution for 20-mer PEI for different protonation states.

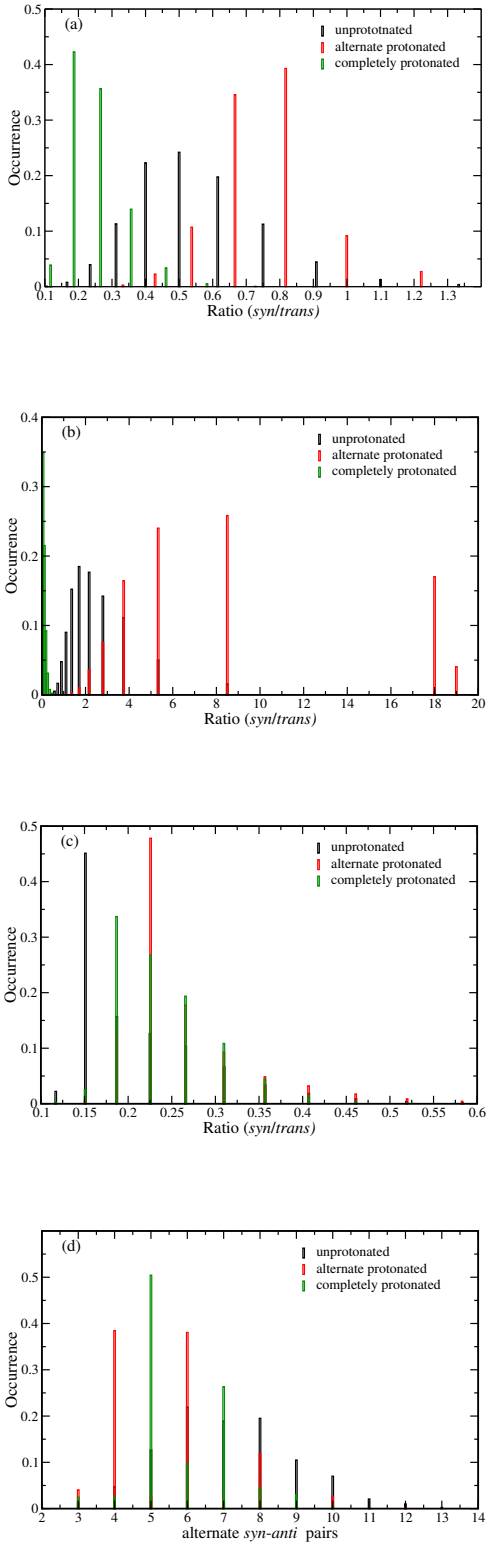
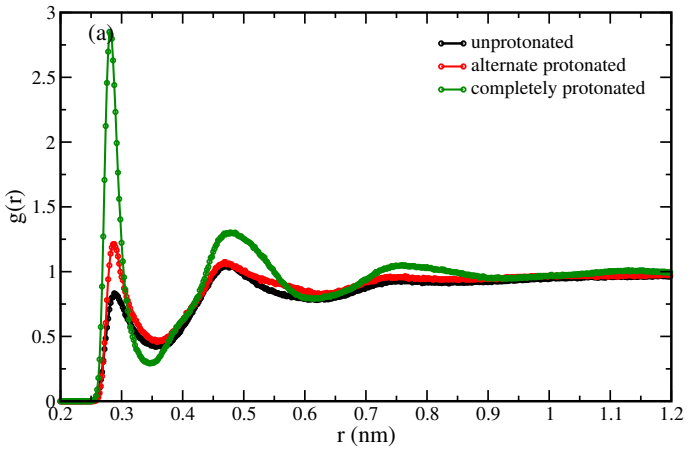
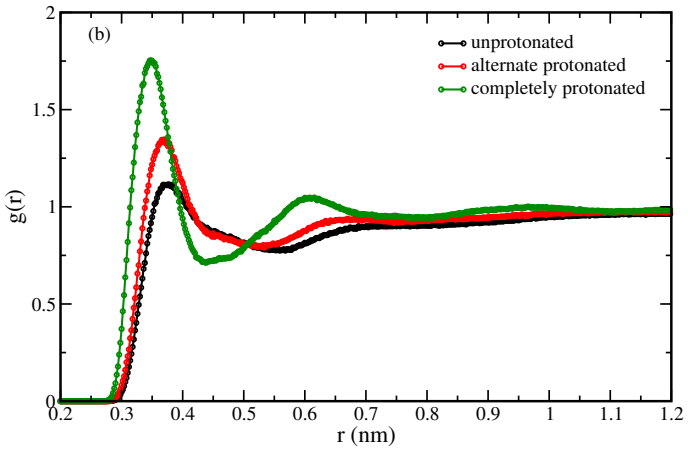


Fig. S7 Distribution of ratio (*syn/anti*) when (a) all, (b) N-C-C-N and (c) C-C-N-C dihedrals were considered. (d) Alternate *syn-anti* occurrences of all the dihedrals for 20-mer PEI.





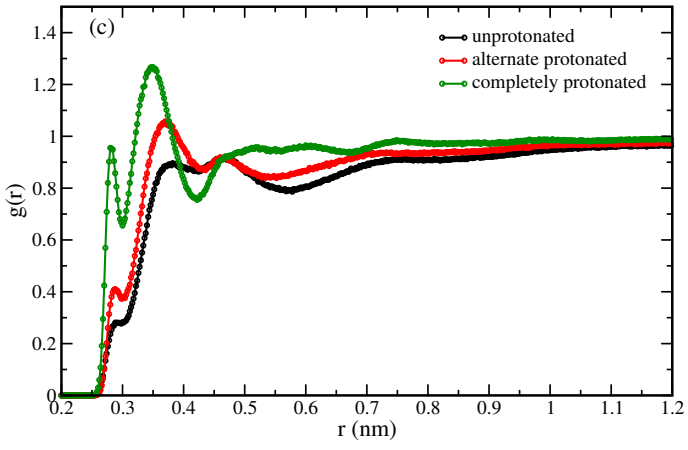
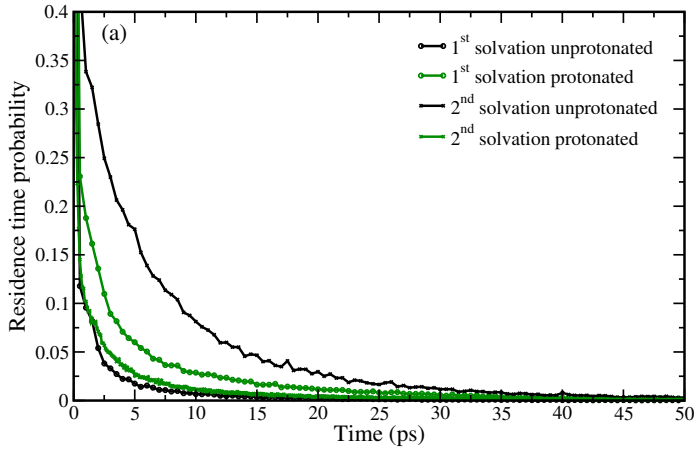
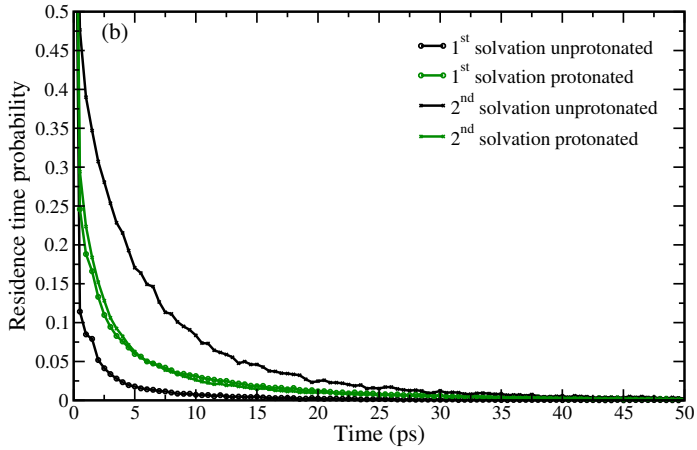


Fig. S8 The pair distribution plot of (a) N of PEI and O of Water, (b) C of PEI and O of Water and (c) N and C of PEI and O of Water for 20-mer PEI.





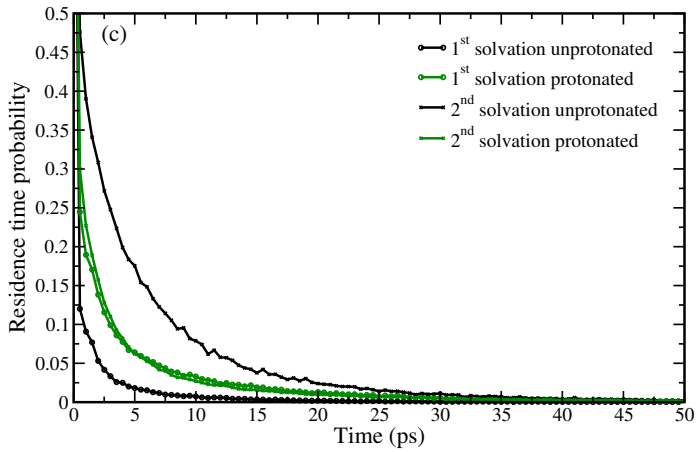


Fig. S9 Residence time probability of the water molecules in different solvation shells of the polymer chain (50-mer) at (a) 310 K (b) 320 K and (c) 330 K.

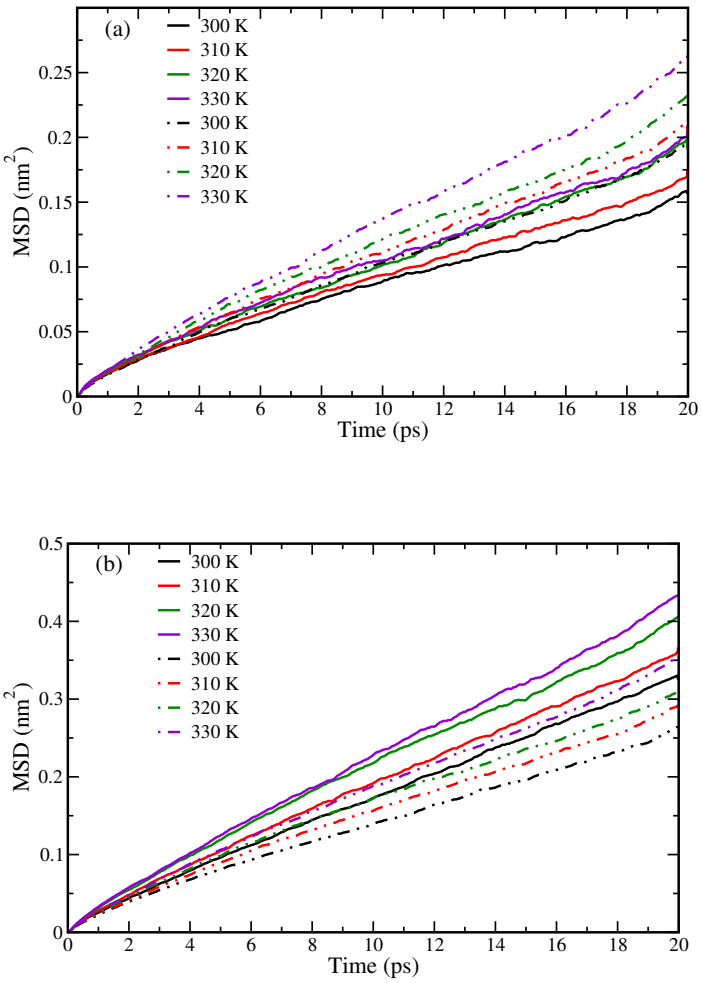


Fig. S10 Mean square displacement of water molecules around the (a) 1^{st} solvation shell, and (b) 2^{nd} solvation shell at different temperatures for unprotonated (solid lines) and protonated (dotted - dashed lines) states of 50-mer PEI.