Effects of Hydration on the Acid-Base Interactions and Secondary Structures of Poly-L-Lysine Probed by ^{15}N and ^{13}C Solid State NMR

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Table S1. ^{15}N chemical shift of liquid spectra

sample	pH	H_2O/Lys	δ (ppm)	half width (Hz)
10	13	0	-16.6	490
11	13	7.3	-13.1	180

Table S2. ^{15}N chemical shift and half width of dry and hydrates samples lyophilized at different pH.

sample	counterion	pH	H2O/Lys	chemical shif signal 1/ppm	chemical shif signal 2/ppm	signal half width /Hz	relative intensities signal 1: signal 2
12	chloride	2	0	4.8	-	460	-
13	chloride	2	0.8	2.2	(-1.2)	500	0.54 : 0.12
14	chloride	2	1.8	1.8	-1.2	400	0.4 : 0.17
15	chloride	2	2.8	1.3	-1.7	350	1:1
16	chloride	2	4.4	0.8	-3.1	110	0.18 : 0.28
17	chloride	4	0	4.4		480	
18	chloride	4	1.2	2.2	-1.0	440	0.49 : 0.18
19	chloride	4	2..6	1.3	-1.7	360	0.20 : 0.22
20	chloride	4	4.0	0.1	-3.5	120	0.22 : 0.4
21	chloride	4	4.8	0.7	-3.1	100	1.24 :2.97
22	chloride	4	5.8	0.5	-3.1	100	0.09 :0.47
23	bromide	4	0	6.2		600	
24	bromide	4	0.7	2.6	-0.5	490	0.40 :0.49
25	bromide	4	0.9	3.5	-0.2	505	0.39 : 0.45

26	bromide	4	2.8	3.8	-2.3	170	0.24 : 0.68
27	bromide	4	3.1	4	-2.3	160	0.16 : 1
28	bromide	4	4.5		-2.9	170	-
29	fluoride	4	0	-8.8	-	650	-
30	fluoride	4	1.6	-8.3	-	240	-
31	fluoride	4	2.7	-8.1	-	180	-
32	fluoride	4	2.8	-8.1	-	180	-
33	fluoride	4	3.7	-7.9	-	140	-
34	fluoride	4	3.8	-7.9	-	140	-
35	fluoride	4	4.8	-7.9	-	130	-
36	chloride	10.3	0	-0.9	-12.5	1200	
37	chloride	10.3	0.3	-5.3	-8.3	590	
38	chloride	10.3	1.8	-6.5	-	460	
39	chloride	10.3	3.1	-7.4	-	190	
40	chloride	10.6	0	-14.5		920	
41	chloride	10.6	0.3	-13.5		790	
42	chloride	10.6	0.6	-12.7		630	
43	chloride	10.6	0.9	-12.1	-8.7	540	0.19 : 0.26
44	chloride	10.6	1.9	-12.8	-9.5	380	0.36 :0. 20
45	chloride	10.6	3.1	-13.0	-9.6	350	0.61 : 0.33
46	chloride	10.6	3.5	-12.2	-9.2	320	0.37 : 0.15

Figure S1. ^{15}N NMR spectra (60.8 MHz) of dry and wet PLL×HCl lyophilized at pH 2. For comparison, the liquid state NMR spectrum of Figure 4b obtained at pH 4 is included.