Electronic Supplementary Information for: Acidity of the Methyne Group of Poly(4-vinylpyridine) leads to Side-chain Protonation in Pyridine.

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DFT modeling.

The geometry optimized structure and natural bond orbital (NBO) charge distribution of the P4VP monomer, the P4VP monomer with protonated polymer side-chain and neighboring liquid pyridine molecule were calculated using the B3LYP hybrid density functional in conjunction with the Pople 6-311++G(d,p) basis set as implemented in the Gaussian-09 package.[1] It was necessary to calculate the charge distributions for singlet, triplet and two doublet states (anion and cation radicals) because the polymer side-chain in pyridinic solution can exist in different electronic states.[2] IR frequencies of the optimized protonated complex were calculated using the PBE1PBE hybrid density functional method[3] in conjugation with the Dunning correlation consistent polarized valence double ξ (cc-pVDZ) basis set.[4]

DFT modeling.

Table S1. NBO charge distributions (in electrons) for singlet (^{1}A) and triplet (^{3}A) states of the polymer side chain and the cation ($^2A^+$) and anion ($^2A^-$) radical states.

	^{1}A	^{3}A	$^2A^+$	$^2A^-$
C_1	0.058	-0.064	0.031	0.024
C_2	-0.251	-0.242	-0.177	-0.270
C_3	0.018	-0.021	0.086	-0.035
C_4	-0.245	-0.241	-0.175	-0.268
C_5	0.060	-0.066	0.036	0.028
H_6	0.184	0.210	0.273	0.157
H_7	0.208	0.212	0.259	0.189
H_8	0.208	0.211	0.259	0.160
H_9	0.185	0.210	0.276	0.157
N_{10}	-0.459	-0.222	-0.004	-0.537
C_{11}	**-0.240**	**-0.248**	**-0.244**	**-0.262**
C_{12}	**-0.368**	**-0.371**	**-0.372**	**-0.387**
H_{13}	0.194	0.193	0.221	0.106
H_{14}	0.189	0.184	0.194	0.158

H_{15}	0.193	0.193	0.213	0.084
C_{16}	-0.575	-0.576	-0.582	-0.587
H_{17}	0.202	0.202	0.190	0.166
H_{18}	0.201	0.200	0.226	0.133
H_{19}	0.193	0.192	0.205	0.133
C_{20}	-0.558	-0.558	-0.563	-0.558
H_{21}	0.201	0.198	0.230	0.198
H_{22}	0.196	0.195	0.203	0.195
H_{23}	0.205	0.205	0.214	0.205

Table S2. Total energy without (E_{tot}) and with (E_{tot}(ZPE)) zero point energy corrections (in au) for singlet (^{1}A) and triplet (^{3}A) states of the polymer sidechain and the cation ($^2A^+$) and anion ($^2A^-$) radical states.

	^{1}A	^{3}A	$^2A^+$	$^2A^-$
E_{tot}	-405.651953	-405. 517421	--405. 327656	--405.63746
E_{tot}(ZPE)	--405.451247	-405.322395	-405.129971	-405.43957

Table S3. IR frequencies (cm^{-1}) and intensities ($km*m^{-1}$) for the protonated side chain pyridine / free pyridine complex. PS-Ch - CH stretch (symm.) in protonated side-chain pyridine ring; PR - CH strech (symm.) in pyridine ring.

N	Freq*	Intens.**	Vibration assighnment***	N	Freq*	Intens.**	Vibration assighnment
1	10.6	0.4		45	1098.8	18.5	HCC bending (symm.) in PR
2	20.8	0.1		46	1116.3	0.2	HCC bending (symm.) in PS-Ch
3	24.7	0.0		47	1124.4	57.7	CCC bending (ssym.) main chain/PS-Ch
4	49.3	0.0		48	1164.1	1.9	HCC bending (asymm.) in PR
5	51.9	0.6		49	1222.7	1.9	CCC bending (assym.) main chain/PS-Ch
6	72.8	1.3		50	1227.0	40.5	HCC bending (symm.) in PS-Ch
7	90.0	5.1		51	1240.8	11.2	HCC bending (symm.) in PR
8	98.2	0.8		52	1283.0	11.8	HCC,HCN bending (asymm.) in PR
9	108.7	0.0		53	1305.3	6.6	CCC bending (asymm.) between main chain and and PS-Ch
10	137.9	0.0		54	1350.3	0.0	HCC, HCN bending (asymm.) in PR
11	251.4	0.7		55	1368.2	0.7	HCC bending (asymm.) in PR
12	310.7	15.5	deformation mode in PS-Ch	56	1392.5	5.0	HCC bending (complete asymm.) in methyl group of main chain
13	363.3	2.1		57	1395.9	13.6	HCC bending (complete symm.) in methyl group of main chain
14	389.5	0.0		58	1436.0	1.0	HNC bending (asymm.) in PS-Ch
15	420.9	2.4		59	1436.0	0.8	HNC bending (asymm.) in PS-Ch
16	459.2	0.1		60	1451.7	1.4	HCC bending (asymm.) in methyl group and in PS-Ch
17	463.9	8.6		61	1455.2	9.5	HCC bending (asymm.) in methyl group of main-chain
18	464.9	1.8		62	1459.2	8.4	HCC bending (asymm.) in methyl group of main-chain

19	486.8	13.8	breathing mode (asymm.) in PS-Ch	63	1467.1	0.4	HCC bending (symm.) in methyl group of main-chain
20	620.8	14.4	breathing mode (asymm.) in PR	64	1480.0	32.9	CC, CN stretch (asymm.) in PR
21	651.5	0.0		65	1519.3	0.7	CC, CN stretch (symm.) in PR
22	659.7	3.7		66	1588.0	71.8	CN stretch (asymm.) in PS-Ch
23	669.5	3.6		67	1661.0	8.8	CC,CN stretch (asymm.) in PR
24	721.0	49.6	HCC (out-of-plane) in PR	68	1675.2	43.6	CC stretch (symm.) in PR
25	723.2	3.5		69	1677.8	2.6	C(main chain)C(PS-Ch) stretch (asymm.)
26	770.0	9.3		70	1683.8	2.3	C(main chain)C(PS-Ch) stretch (symm.)
27	779.3	0.0		71	1764.4	297.2	CC stretch (symm.) PS-Ch
28	798.4	15.2		72	3008.3	33.7	CH stretch (complete asymm.) in methyl group of main-chain
29	818.5	100.5	HNC bending (out-of- plane) in PS-Ch	73	3013.2	246.1	CH stretch (complete symm.) in methyl group of main-chain
30	902.9	0.0		74	3056.0	69.5	CH stretch (asymm.) in methyl group of main-chain
31	934.0	0.9		75	3059.0	4.4	CH stretch (asymm.) in methyl group of main-chain
32	950.5	1.0		76	3159.7	25.4	CH stretch (asymm.) in methyl group of main-chain
33	953.1	0.1		77	3160.5	16.5	CH stretch (symm.) in methyl group of main-chain
34	956.0	0.7	HCC bending in methyl group of main-chain	78	3192.5	6.0	CH stretch (asymm.) in PR
35	968.6	0.0	HCC bending (out-of-plane.) in PR	79	3196.8	6.9	CH stretch (asymm.) in PR
36	976.6	2.1	Bending in methyl group of main-chain	80	3215.8	1.0	CH stretch (asymm.) in PR
37	997.4	24.6	breathing in PS-Ch	81	3221.1	3.1	CH stretch (assym.) in PS-Ch
38	1011.6	0.0	HCC bending (out-of- plane) in PR	82	3222.3	2.9	CH stretch (assym.) in PS-Ch
39	1026.5	0.0	HCC bending out of plane in PS-Ch	83	3234.1	9.5	CH stretch (asymm.) in PR
40	1027.7	41.0	CCC, CCN. NCC bending in of PR	84	3240.7	9.7	CH stretch (symm.) in pyridine ring (PR)
41	1045.3	34.8	CCC, CCN. NCC bending in PS-Ch	85	3247.5	27.4	CH stretch (assym.) in PS-Ch
42	1059.1	0.1	breathing mode in PR	86	3249.0	1.1	CH stretch (symm.) in protonated side-chain pyridine ring (PS-Ch)
43	1070.2	0.7	HCC bending (symm.) in methyl group of main chain	87	3382.8	2286.9	N-H stretch
44	1093.9	0.1	HCC, HCN bending (symm.) in PR				

* cm^{-1}

** $km*mol^{-1}$ [http://akira.ruc.dk/~spanget/IR_intensity_.pdf]

***Assignment of vibrational modes for selected vibrations.

References:

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4 T.H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007.