Supplementary Information for

Structural Analyses of Blended Nafion/PVDF Electrospun Nanofibers

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Figure SI-1. HR-TGA profiles of $[P/N_{0.9}]^X$, $[N]^C$, $[P]^M$ and $[P]^{MM}$ conducted under an air atmosphere with all samples either in the dry state (left) or wet state (right). The profiles given as the first derivative weights are shown in the bottom panels.

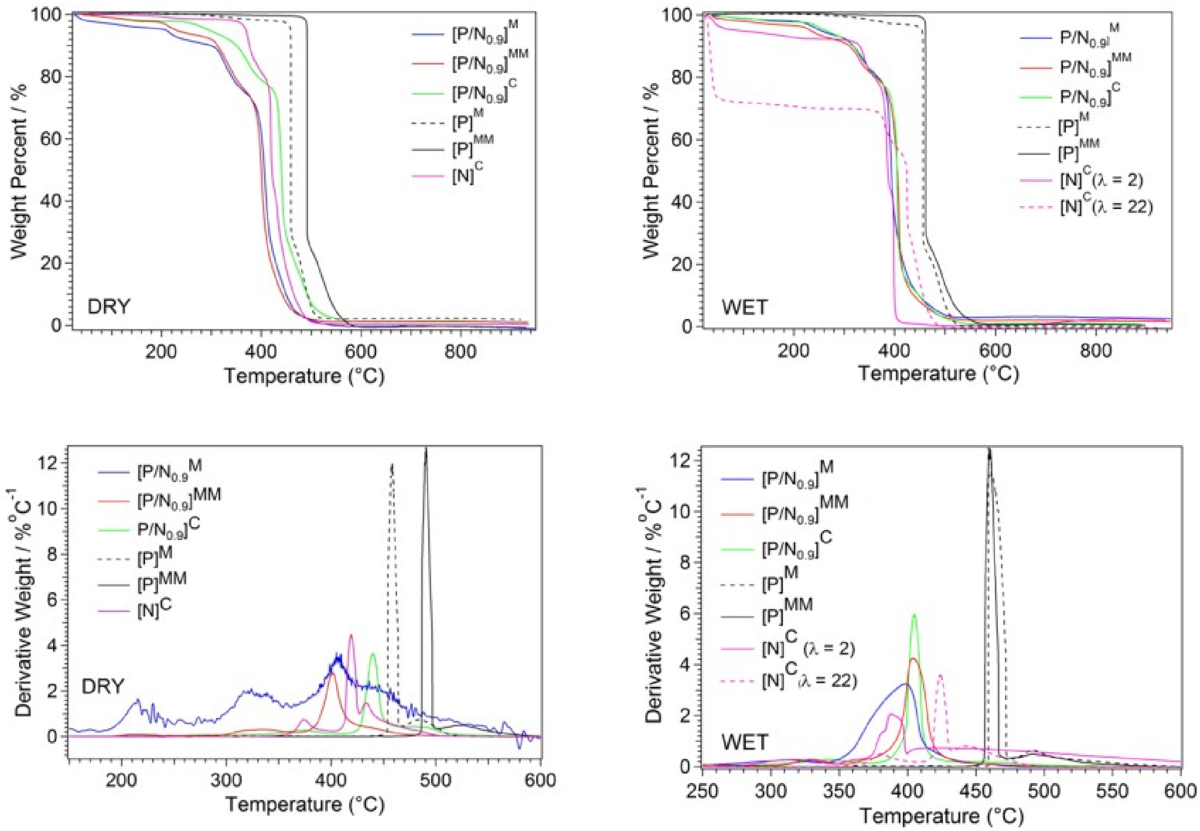
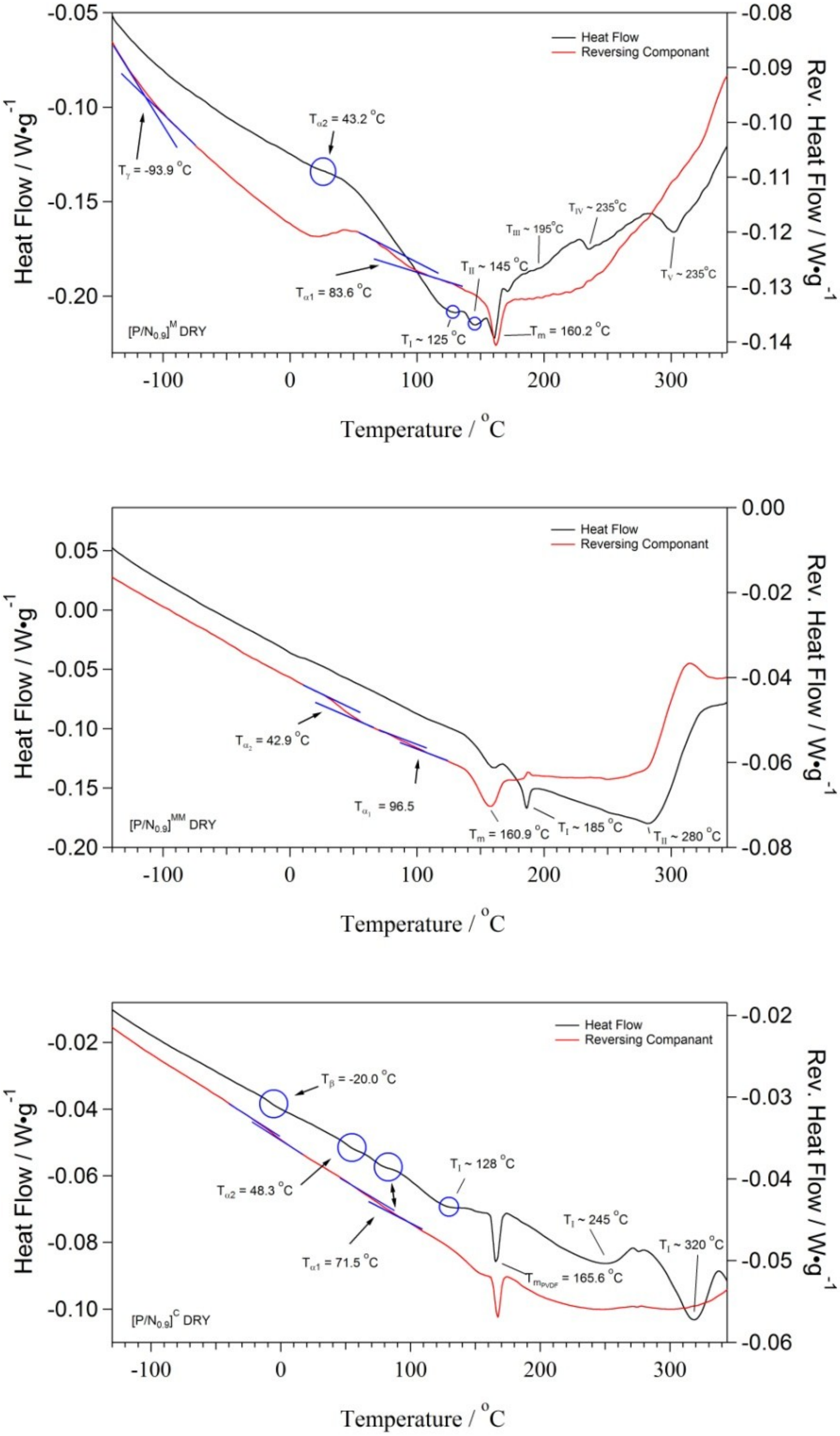
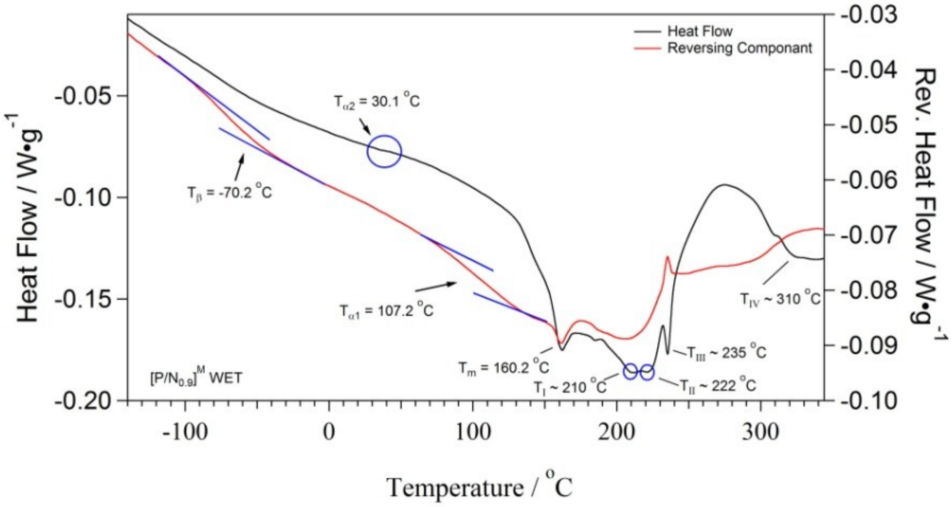
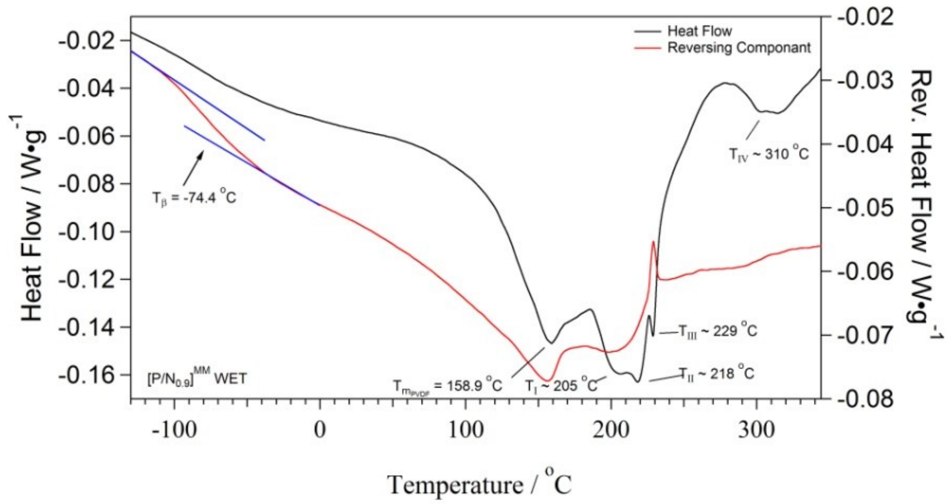
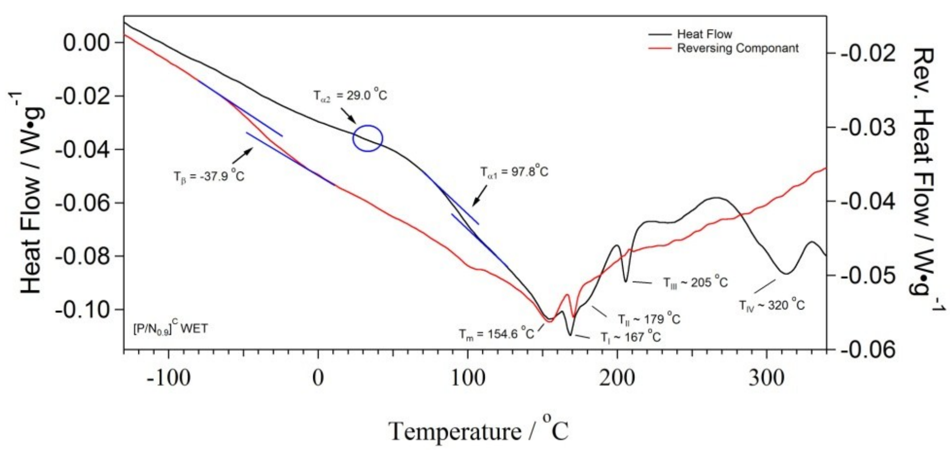


Figure SI-2. TMDSC profiles of $[P/N_{0.9}]^X$ in the dry and the wet state




Heat Flow
Reversing Componant
Heat Flow / W•g-1
Rev. Heat Flow / W•g-1
Temperature / °C
Tα2 = 30.1 °C
Tβ = -70.2 °C
Tα1 = 107.2 °C
Tm = 160.2 °C
TI ~ 210 °C
TII ~ 222 °C
TIII ~ 235 °C
TIV ~ 310 °C
[P/N0.9]M WET


Heat Flow
Reversing Componant
Heat Flow / W•g-1
Rev. Heat Flow / W•g-1
Temperature / °C
Tβ = -74.4 °C
TmPVDF = 158.9 °C
TI ~ 205 °C
TII ~ 218 °C
TIII ~ 229 °C
TIV ~ 310 °C
[P/N0.9]MM WET


Heat Flow
Reversing Componant
Heat Flow / W•g-1
Rev. Heat Flow / W•g-1
Temperature / °C
Tα2 = 29.0 °C
Tβ = -37.9 °C
Tα1 = 97.8 °C
Tm = 154.6 °C
TI ~ 167 °C
TII ~ 179 °C
TIII ~ 205 °C
TIV ~ 320 °C
[P/N0.9]C WET

Equation SI-3. The equation used to elaborate the fraction of β-phase PVDF, $F(\beta)$, in $[P]^{M}$ and $[P]^{MM}$. (1)

$$F(\beta) = \frac{I_{840}(\beta)}{1.26 I_{762}(\alpha) + I_{840}(\beta)}$$

Figure SI-4. ATR-FTIR spectra for $[P]^{M}$ and $[P]^{MM}$ in the range 400 ÷ 4000 cm^{-1}.

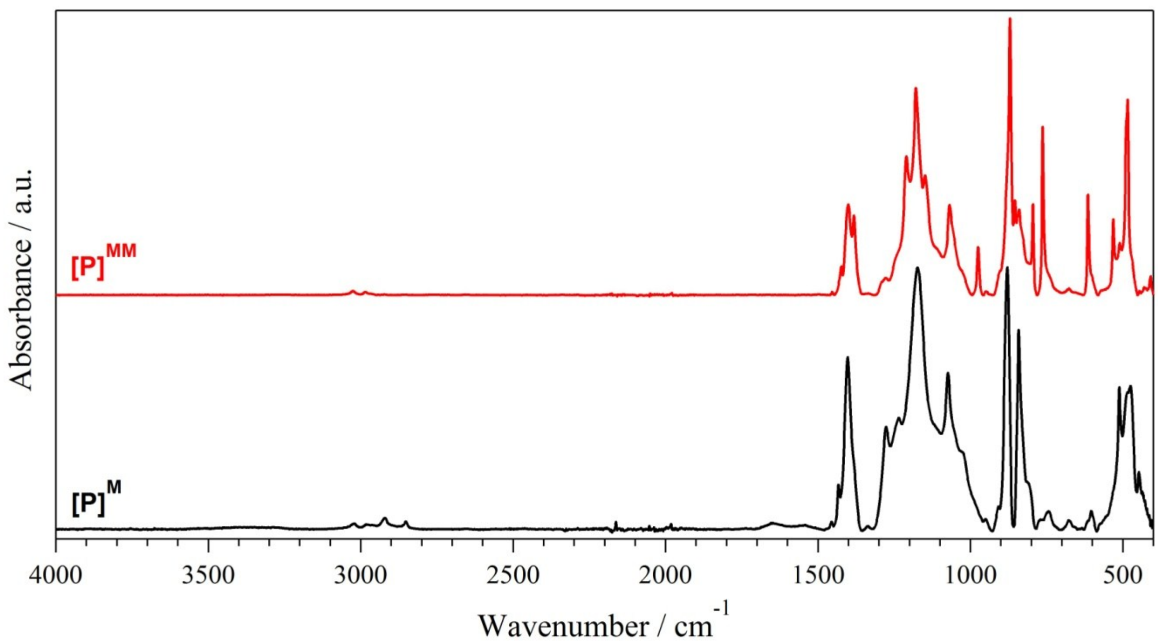


Table SI-5. ATR-FTIR assignments for $[P]^M$ (β-$[P]^M$) (Observed frequencies, calculated frequencies and Potential Energy Distribution (PED) assignments).

Observed frequencies /cm^{-1}	Calculated frequencies /cm^{-1}	Assignments PED[a](%)
3017 (vw)	3029	$\nu_a(CH_2)(99)$
2958 (vw)		
2918 (vw)	2980	$\nu_s(CH_2)(99)$
2849 (vw)		
1430 (w)	1423	$\delta_s(CH_2)(81)$
1400 (s)	1396	$\omega(CH_2)(58)$- $\nu_a(CC)(35)$
1274 (w)	1286	$\nu_s(CF_2)(40)$- $\nu_s(CC)(22)$+ $\delta(CCC)(15)$
1232 (m) 1171 (vs)	1182	$\nu_a(CF_2)(64)$- $r(CF_2)(21)$+ $r(CH_2)(15)$
1071 (s) 1049 (m)	1065	$\nu_a(CC)(54)$- $\omega(CF_2)(22)$+ $\omega(CH_2)(24)$
1019 (m)		
974 (vw)	983	$t(CH_2)(100)$
946 (vw)		
904 (vw) 876 (vs)	879	$\nu_s(CF_2)(54)$+ $\nu_s(CC)(18)$
839 (s) 806 (vw)	825	$r(CH_2)(60)$- $\nu_a(CF_2)(31)$
509 (m)	508	$\delta(CF)(98)$
480 (m)	470	$\omega(CF_2)(92)$
443 (w)	443	$r(CF_2)(74)$+$r(CH_2)(26)$
-	262	$t(CF_2)(100)$
-	72	Vibrational lattice mode

[a]The values obtained by the normal coordinate treatment for a single chain.

Relative intensity; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Symmetry coordinates; ν_s, symmetric stretching; ν_a, antisymmetric stretching; δ, bending; ω, wagging; t, twisting; r, rocking. The + or – denotes the phase relation among the symmetry coordinates.

Table SI-6. ATR-FTIR assignments for $[P]^{MM}$ ((α+β)-$[P]^{MM}$(Observed frequencies, calculated frequencies and Potential Energy Distribution (PED) assignments). (2)

Observed frequencies /cm^{-1}	Calculated frequencies for β /cm^{-1}	Calculated frequencies for α /cm^{-1}	Assignments for β PED[a](%)	Assignments for α PED[b](%)
2985 (vw)	2980	2980	$\nu_s(CH_2)$(99)	CH(100)
1423 (vw)	1423	1424	$\delta_s(CH_2)$(81)	CHH(73)+CCH(17)
1401 (w)	1396		$\omega(CH_2)$(58)- ν_a(CC)(35)	
1382 (w)		1383		CCH(53)+CC(18)+CF(17)
1277 (vw)	1286	1285	$\nu_s(CF_2)$(40)- ν_s(CC)(22)+ δ(CCC)(15)	CF(77)+CCF(24)+CC(13)
1240(sh,vw) 1211 (m)		1251		CF(68)+CCH(36)
1178 (s) 1148 (m)	1182	1175		CF(41)+CCH(38)+CC(24)+CCC(21)
1068 (w)	1065		ν_a(CC)(54)- $\omega(CF_2)$(22)+ $\omega(CH_2)$(24)	
975 (vw)		961		CCH(102)
948 (vw)		948		CCH(103)
902 (sh,vw)		909		CC(47)+CCH(18)
882 (sh,vw)	879		$\nu_s(CF_2)$(54)+ ν_s(CC)(18)	
870 (vs) 853 (w)		870		CC(31)+CF(21)+CCC(13)
840 (w) 833 (sh,w) 827 (sh,w)	825	825	$r(CH_2)$(60)- $\nu_a(CF_2)$(31)	CCH(54)+CF(18)
795 (m)		811		CCH(72)
762 (s)		757		CCF(35)+CF(29)+CCC(23)
615 (m)		601		CFF(24)+CCF(24)
531 (w)		517		CFF(66)
510 (w)	508		δ(CF)(98)	
484 (s)	470		$\omega(CF_2)$(92)	
445 (b,vw)	443		$r(CF_2)$(74)+$r(CH_2)$(26)	
430 (b,vw)		420		CCF(52)
409 (vw)		400		CCF(84)

[a]The values obtained by the normal coordinate treatment for a single chain.
Relative intensity; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.
Symmetry coordinates; ν_s, symmetric stretching; ν_a, antisymmetric stretching; δ, bending; ω, wagging; t, twisting; r, rocking. The + or – denotes the phase relation among the symmetry coordinates.

Figure SI-7. ATR-FTIR spectra for $[P/N_{0.9}]^X$ (X = M, MM and C) and $[P]^M$ in the dry state and $[N]^C$ ($\lambda = 0$) in the range between 400 and 4000 cm^{-1}.

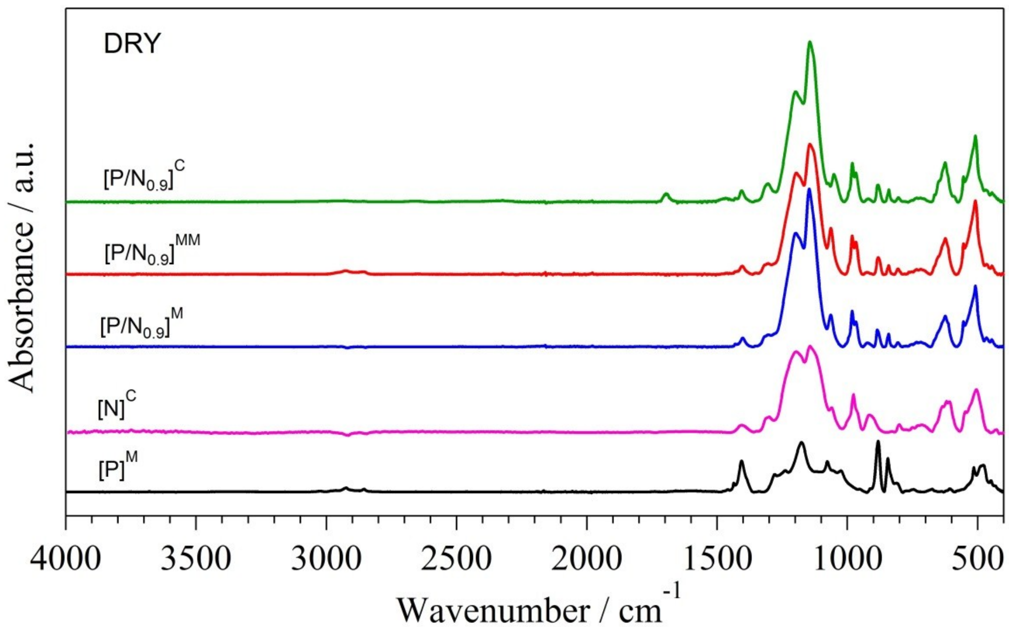


Figure SI-8. ATR-FTIR spectra for $[P/N_{0.9}]^X$ (X = M, MM and C) and $[P]^M$ in the wet state and $[N]^C$ ($\lambda = 22$) in the range between 400 and 4000 cm^{-1}.

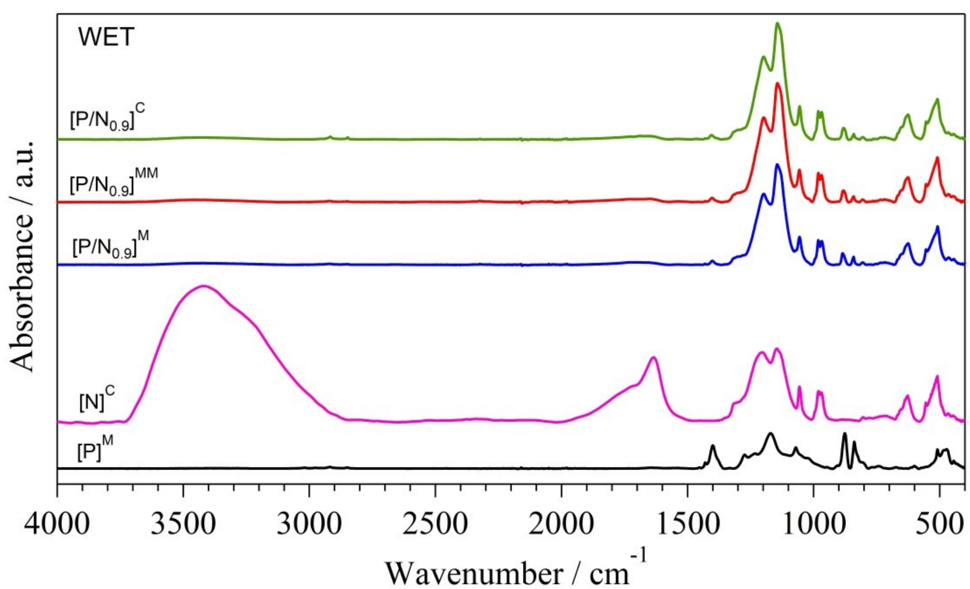


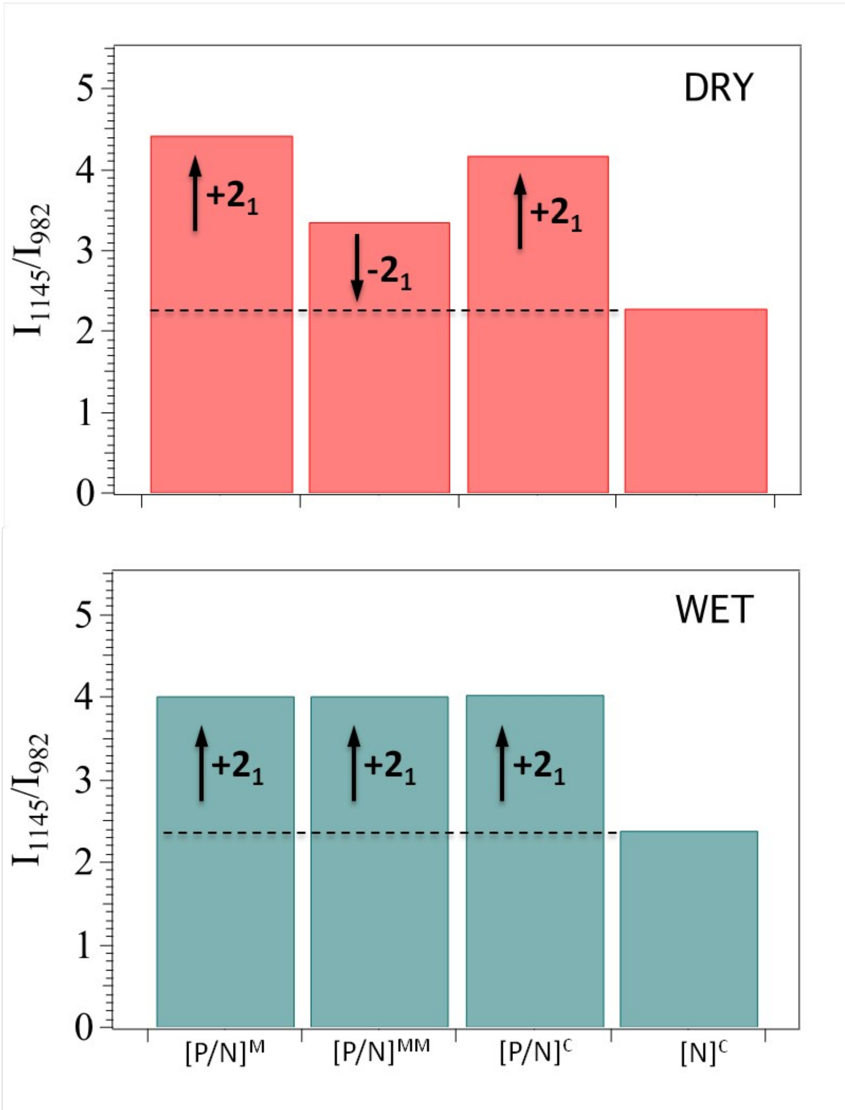
Table SI-9. ATR-FTIR assignments for $[P]^M$, $[P/N_{0.9}]^X$ (X = M, MM and C), $[N]^C$ ($\lambda = 0$) and $[N]^C$ ($\lambda = 2$).

Observed frequencies^a /cm^{-1}							
$[P]^M$	$[P/N_{0.9}]^M$	$[P/N_{0.9}]^{MM}$	$[P/N_{0.9}]^C$	$[N]^C$ ($\lambda = 0$)	$[N]^C$ ($\lambda = 2$)	**Assignments^b**	**Ref.**
					3952(m,sh)	$\nu(\text{-}CF_2\cdots H_2O\cdots F_2C\text{-})$	[6]
					3419(vs)	$\nu_{as}(H_2O)$	[6]
					3222(s)	$\nu_s(H_2O)$	[6]
					3000(w,sh)	$\nu_{as}(H_3O^+)$	[6]
3017 (vw)						$\nu_a(CH_2)(99)$	[8,9]
2958 (vw)						$\nu_s(CH_2)(99)$	[8.9]
2918 (vw)		2928(vw)	2930(vw)			$\nu_s(CH_2)(99)$	[8,9]
2849 (vw)		2858(vw)	2855(vw)			$\nu_s(CH_2)(99)$	[8.9]
					1726(w)	$\delta[H_3O^+\cdots(H_2O)_n]$	[6]
					1633(m)	$\delta(H_2O)_n$	[6]
	1540 (vw)	1540 (vw)	1545 (vw)			$\delta(H_2O)_2$	[10]
1430 (w)	1431(vw)	1431	1431(vw)			$\delta_s(CH_2)(81)$	[8,9]
				1410(vw)		$\nu_s(SO_3H)$	[6]
1400 (s)	1402(vw)	1404	1406(vw)			$\omega(CH_2)(58)\text{-}\nu_a(CC)(35)$	[8,9]
	1353(vw)	1352			1351(vw,sh)	15_7: $\nu(CC)$	[7]
	1316(sh,vw)	1317		1321(w,sh)	1315(w,sh)	10_3: $\nu(CC)$	[7]
	1304(vw)	1305	1305(vw)	1306(w)	1301(w)	10_3: $\nu(CC)$	[7]
1274 (w)	1279(sh,vw)					$\nu_s(CF_2)(40)\text{-}\nu_s(CC)(22)+\delta(CCC)(15)$	[8,9]
				1238(s,sh)		15_7: $\nu_{as}(CF_2)$	[7]
1232 (m)		1229(sh,vw)				$\nu_a(CF_2)(64)\text{-}r(CF_2)(21)+r(CH_2)(15)$	[8,9]
	1199(s)	1197(s)	1199(s)	1203(vs)	1203(vs)	15_7: $\nu_{as}(CF_2)$	[7,8,9]
				1189(vs,sh)		10_3: $\nu_s(CF_2)$	[7]
1171 (vs)	1181(sh,s)	1180(sh,s)	1183(sh,s)			$\nu_a(CF_2)(64)\text{-}r(CF_2)(21)+r(CH_2)(15)$	[8,9]
	1146(vs)	1145 (vs)	1145 (vs)	1149(vs)	1148(vs)	15_7: $\nu_s(CF_2)$	[7,8,9]
	1131(sh,vs)	1132(sh,vs)	1132(sh,vs)	1112(vs,sh)	1132(vs,sh)	10_3: $\nu_{as}(CF_2)$	[7]
1071 (s)	1064(w)	1064(w)	1073 (vw)	1064(w)	1057(m)	$\nu_s(SO_3^-)$	[11]
1049 (m)			1052 (vw)			$\nu_a(CC)(54)\text{-}\omega(CF_2)(22)+\omega(CH_2)(24)$	[8,9]
1019 (m)		994(sh,vw)	993(sh,vw)	995(w,sh)	993(w,sh)	$\nu_{as}(COC)$tip	[6]
	982(w)	982(w)	982(w)	982(m)	983(m)	$\nu_{as}(COC)$bb	[6]
974 (vw)	967(vw)	967(w)	967 (vw)	967(w,sh)	970(m)	$\nu_s(COC)$tip	[6]
904 (vw)	923(vw) 885(vw)	925(vw) 881(vw)	920(vw) 882(vw)	920(w)		$\delta(SOH)$	[6]
876 (vs)						$\nu_s(CF_2)(54)+\nu_s(CC)(18)$	[8,9]
839 (s)	842(vw)	845(sh,vw) 842(vw)	841(vw)			$r(CH_2)(60)\text{-}\nu_a(CF_2)(31)$	[8,9]
806 (vw)	806(vw)	805(vw)	804(vw)	806(vw)	805(vw)	$\delta(CCF)$, $\delta(COC)$, $\nu(CS)$	[6]
	717(vw)	718(vw)	726(vw) 720(vw) 718(vw)	719(vw)		$\nu(CF_2)$, $\nu(CF_3)$, $\delta(CF)$	[6]
	625(vw)	624(w)	632(sh,vw) 625(w)	625(m)		$\omega(CF_2)$, $\omega(CF_3)$, $\nu(CS)$, $\delta(CF)$	[6]
509 (m)	509(vw)	509(m)	509(w)	511(m)		$r(CF_2)$, $r(CF_3)$, $\delta(OSO)$	[6]
480 (m)		490(sh,vw)	486(sh,vw)			$\omega(CF_2)(92)$	[8,9]
443 (w)	445(vw)	445(vw)	445 (vw)			$r(CF_2)(74)+r(CH_2)(26)$	[8,9]

a: Relative intensities of observed bands are reported in parentheses: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; b: broad;

b: ν: stretching; δ: bending; ω: wagging; r: rocking; as: antisymmetric mode; s: symmetric mode; tip: mode associated to the ether linkage closest to the sulfonic acid group; bb: mode associated to the ether linkage closest to the backbone.

Figure SI-10. Calculated contribution from the 2_1 Nafion conformation in dry $[P/N_{0.9}]^x$ (top) and wet $[P/N_{0.9}]^x$ (bottom). Assuming the 15_7 contribution remains constant between $[P/N_{0.9}]^X$ samples, we calculate the 2_1 contribution using the ratio between I_{1145} (the intensity of $[N]^C$ 2_1: $\nu_s(CF_2)$ + 15_7 : $\nu_s(CF_2)$) and I_{982} (the intensity of ν_{as}(COC)tip vibrational mode), the latter found to be only slightly affected by the $[P/N]^X$ preparation method. The 2_1 contributions are shown as the excess to the 15_7 contributions with respect to Nafion which is comprised solely of 15_7 in the calculation



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