

Supporting Information

A ToF-SIMS study of the deuterium - hydrogen exchange induced by ammonia plasma treatment of polyolefins

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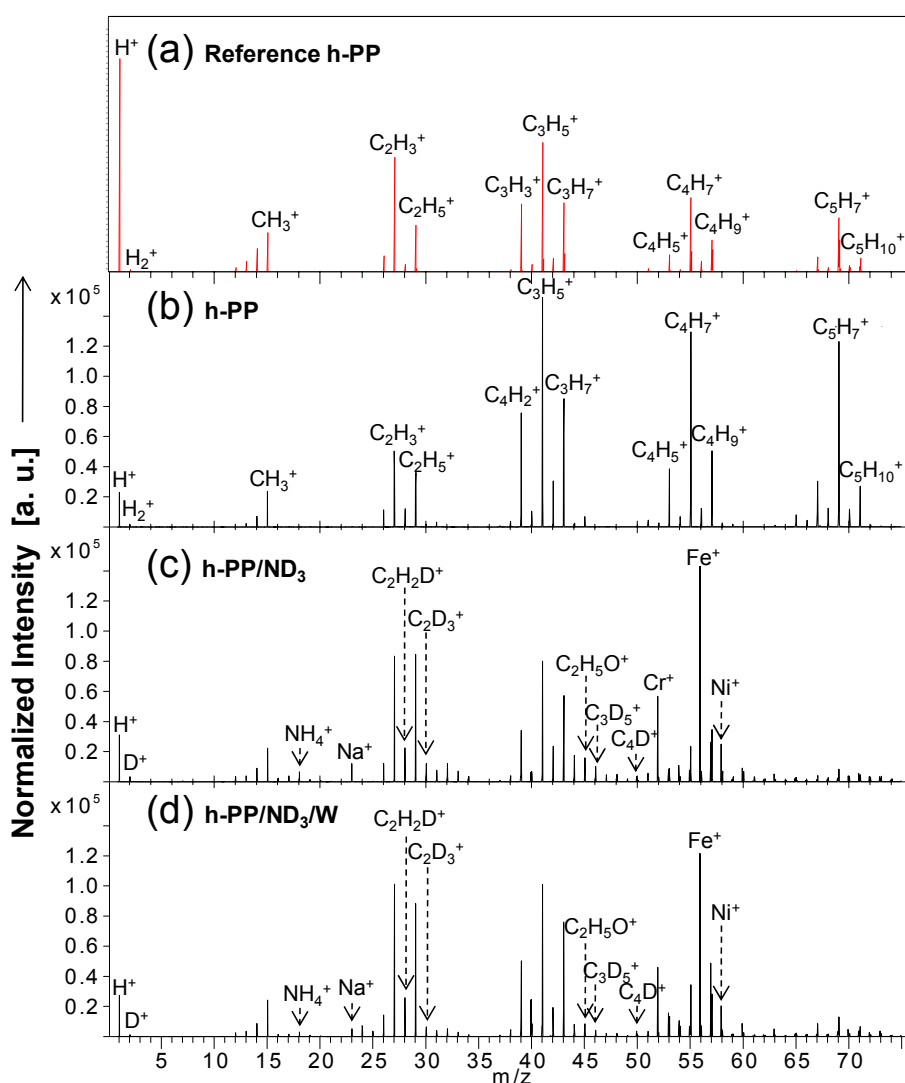


Figure S1 Positive ToF-SIMS spectra for h-PP (b) before and after (c) ND_3 plasma treatment, and (d) post-plasma washing. The reference h-PP spectrum (a) was taken from *The Static SIMS Library*.³⁴

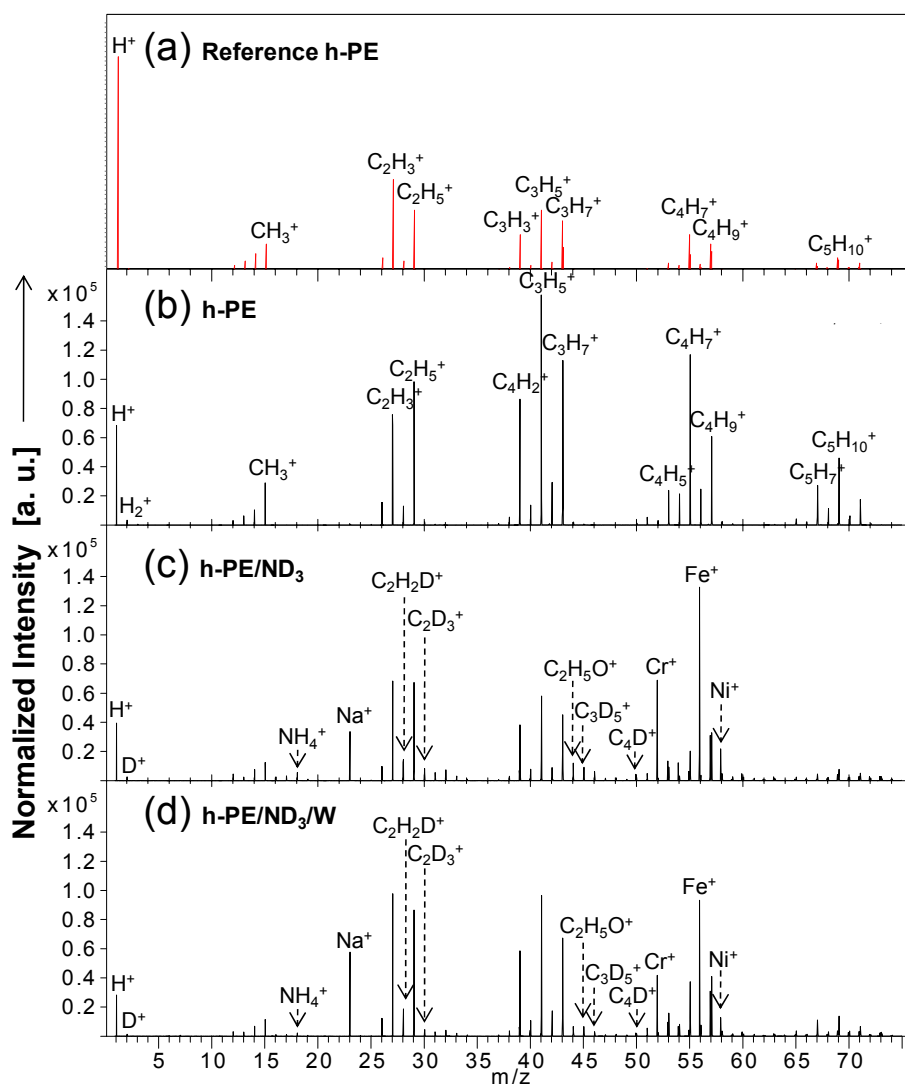


Figure S2 Positive ToF-SIMS spectra for h-PE (b) before and after (c) ND₃ plasma treatment, and (d) post-plasma washing. The reference h-PE spectrum (a) was taken from *The Static SIMS Library*.³⁴

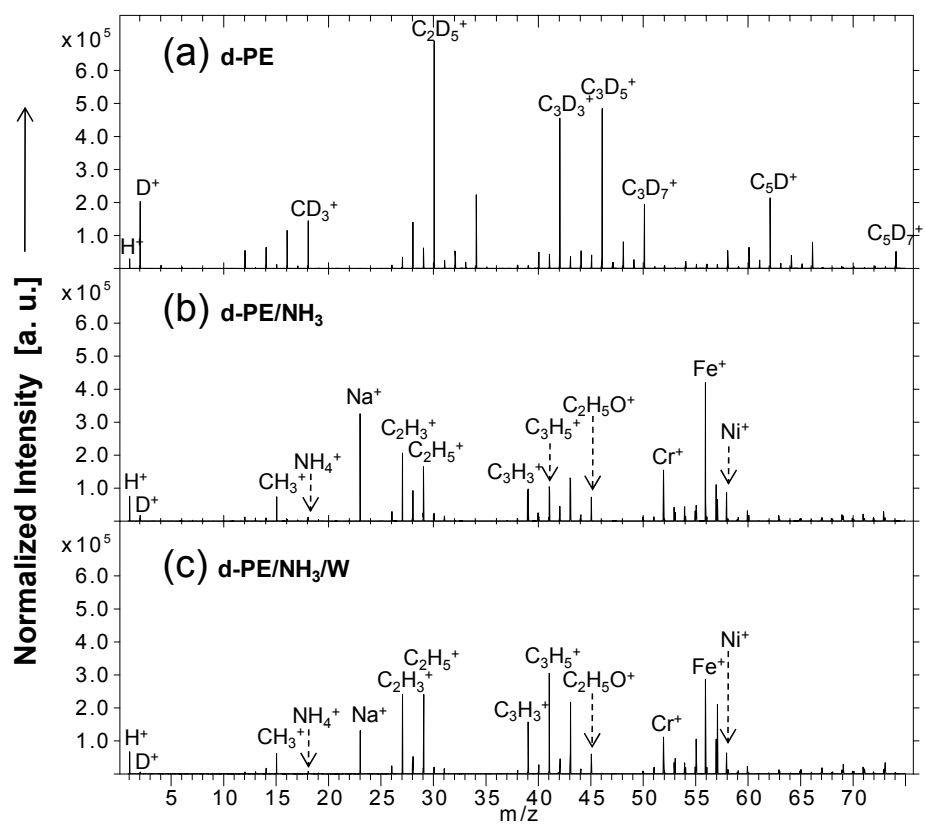


Figure S3 Positive ToF-SIMS spectra for d-PE (a) before and after (b) NH_3 plasma treatment, and (c) post-plasma washing.

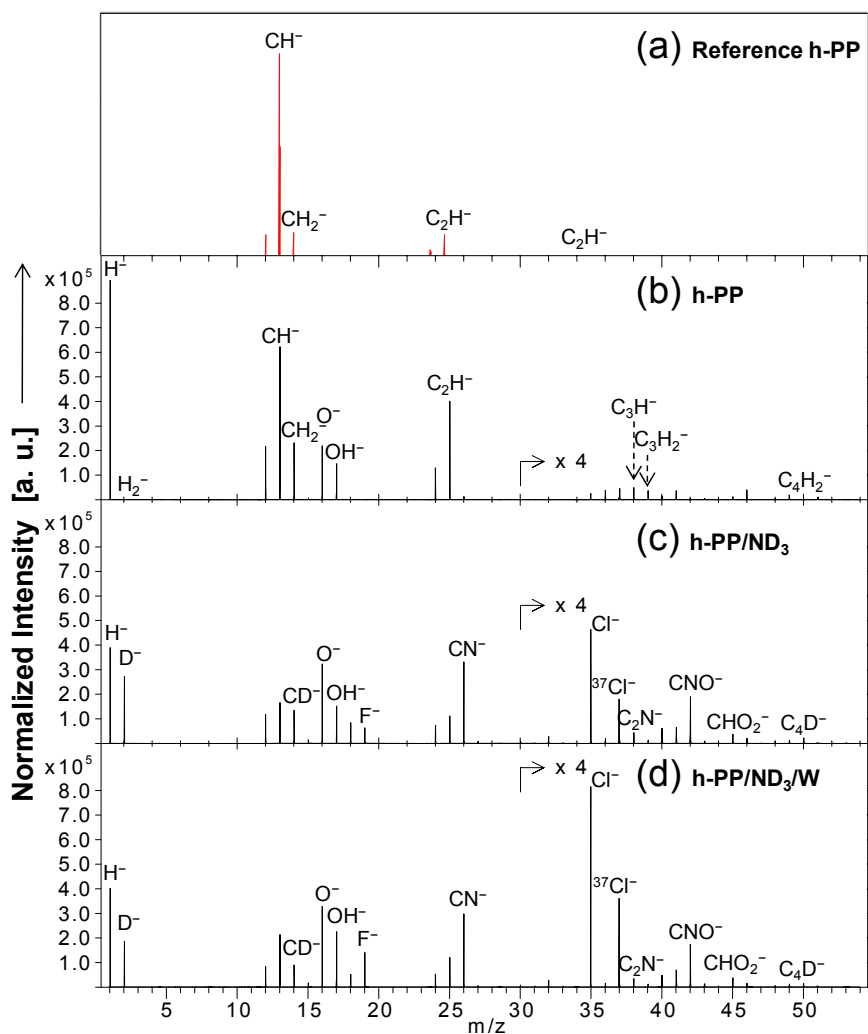


Figure S4 Negative ToF-SIMS spectra for h-PP (b) before and after (c) ND₃ plasma treatment, and (d) post-plasma washing. The reference h-PP spectrum (a) was taken from *The Static SIMS Library*.³⁴

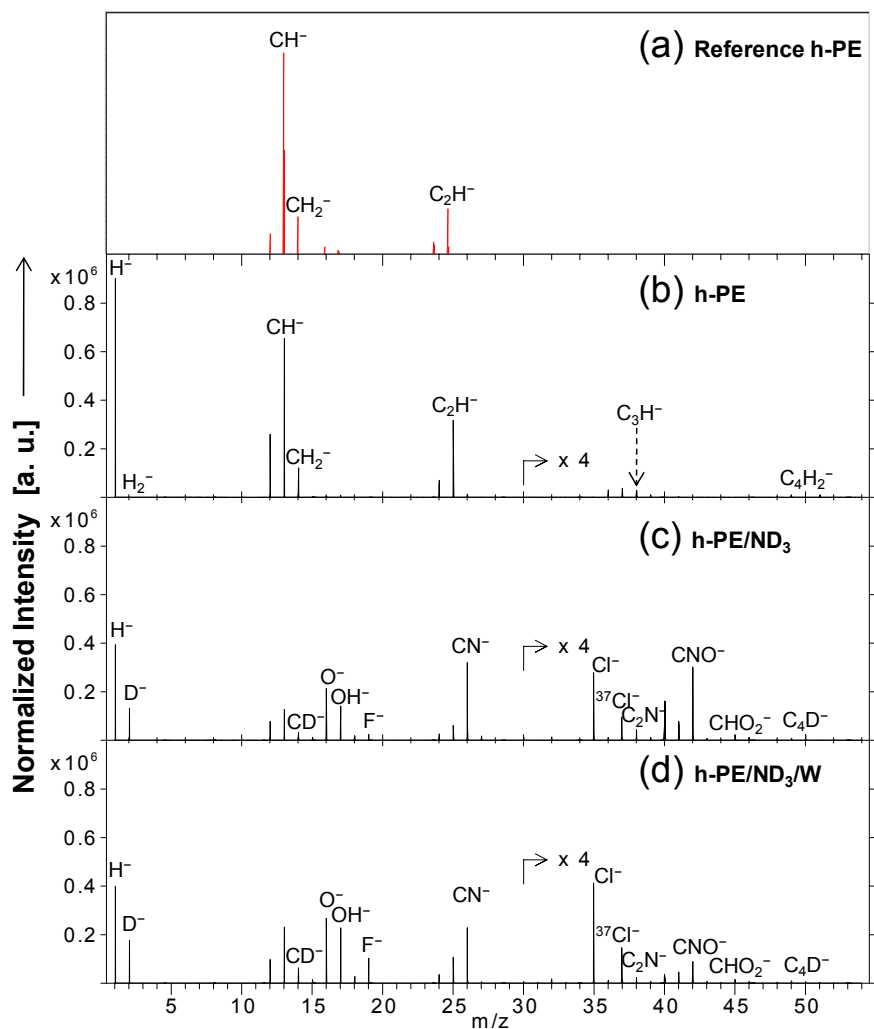


Figure S5 Negative ToF-SIMS spectra for h-PE (b) before and after (c) ND_3 plasma treatment, and (d) post-plasma washing. The reference h-PE spectrum (a) was taken from *The Static SIMS Library*.³⁴

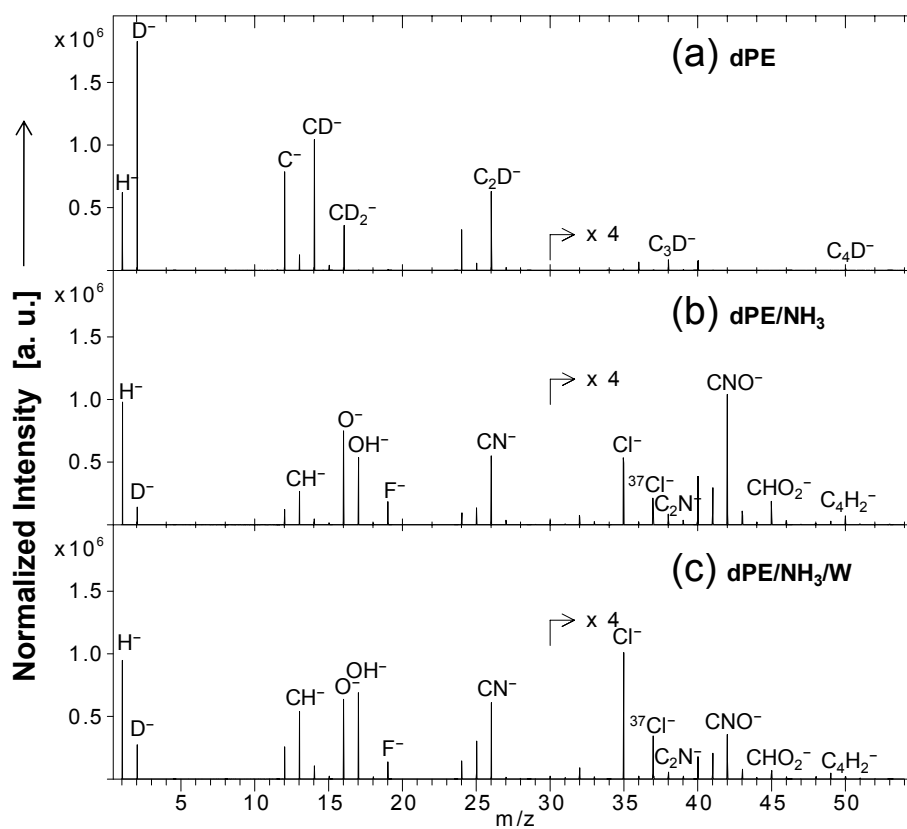


Figure S6 Negative ToF-SIMS spectra for d-PE (a) before and after (b) NH_3 plasma treatment, and (c) post-plasma washing.

Table S1 D-H and H-D exchange related fragments for ND₃ plasma-treated h-PP and h-PE, and NH₃ plasma-treated d-PE samples, respectively, in their positive ToF-SIMS spectra.

Mass <i>m/z</i>	PP	Species PE	dPE
1			H ⁺
2	D ⁺	D ⁺	H ₂ ⁺
3	HD ⁺	HD ⁺	
13			CH ⁺
14			CH ₂ ⁺
15			CH ₃ ⁺
18	CD ₃ ⁺	CD ₃ ⁺	
27			C ₂ H ₃ ⁺
28	C ₂ H ₂ D ⁺ (C ₂ D ₂ ⁺)	C ₂ H ₂ D ⁺ (C ₂ D ₂ ⁺)	C ₂ DH ₂ ⁺ (C ₂ H ₄ ⁺)
29	C ₂ H ₃ D ⁺		C ₂ H ₅ ⁺ (C ₂ DH ₃ ⁺)
30	C ₂ D ₃ ⁺ (C ₂ H ₂ D ₂ ⁺ , C ₂ H ₄ D ⁺)	C ₂ D ₃ ⁺ (C ₂ H ₂ D ₂ ⁺ , C ₂ H ₄ D ⁺)	
31	C ₂ H ₃ D ₂ ⁺ (C ₂ HD ₃ ⁺)	C ₂ H ₃ D ₂ ⁺ (C ₂ HD ₃ ⁺)	
32	C ₂ H ₂ D ₃ ⁺ (C ₂ D ₄ ⁺)		
33	C ₂ HD ₄ ⁺	C ₂ HD ₄ ⁺	
34	C ₂ D ₅ ⁺	C ₂ D ₅ ⁺	
39			C ₃ H ₃ ⁺
41			C ₃ H ₅ ⁺ (C ₃ DH ₃ ⁺)
43			C ₃ H ₇ ⁺ (C ₃ DH ₅ ⁺ , C ₃ D ₂ H ₃ ⁺)
45	C ₃ HD ₄ ⁺ (C ₃ H ₃ D ₃ ⁺ , C ₃ H ₅ D ₂ ⁺)		
46	C ₃ D ₅ ⁺ (C ₃ H ₂ D ₄ ⁺ , C ₃ H ₄ D ₃ ⁺)		
49	C ₃ HD ₆ ⁺		
50			C ₄ H ₂ ⁺
51			C ₄ H ₃ ⁺ (C ₄ HD ⁺)
52			C ₄ DH ₂ ⁺ (C ₄ H ₄ ⁺)
53			C ₄ H ₅ ⁺ (C ₄ DH ₃ ⁺ , C ₃ D ₂ H ⁺)
54			C ₄ DH ₄ ⁺ (C ₄ H ₆ ⁺ , C ₄ D ₂ H ₂ ⁺)
55			C ₄ H ₇ ⁺ (C ₄ DH ₅ ⁺ , C ₄ D ₂ H ₃ ⁺)
56			C ₄ D ₂ H ₄ ⁺ (C ₄ D ₃ H ₂ ⁺ , C ₄ DH ₆ ⁺ , C ₄ H ₈ ⁺)
57			C ₄ H ₉ ⁺ (C ₄ DH ₇ ⁺ , C ₄ D ₂ H ₅ ⁺)
61			C ₅ H ⁺
62			C ₅ H ₂ ⁺
63	C ₅ HD ⁺	C ₅ HD ⁺	C ₅ H ₃ ⁺
64	C ₅ DH ₂ ⁺ (C ₅ D ₂ ⁺)		C ₅ DH ₂ ⁺ (C ₅ H ₄ ⁺)
65			C ₅ H ₅ ⁺ (C ₄ DH ₃ ⁺ , C ₄ D ₂ H ⁺)
66			C ₅ D ₂ H ₂ ⁺ (C ₅ DH ₄ ⁺ , C ₅ H ₆ ⁺)
67			C ₅ H ₇ ⁺ (C ₅ DH ₅ ⁺ , C ₅ D ₂ H ₃ ⁺)
69			C ₅ H ₉ ⁺

Table S2 D-H and H-D exchange related fragments for ND₃ plasma-treated h-PP and h-PE, and NH₃ plasma-treated d-PE samples, respectively, in their negative ToF-SIMS spectra.

Mass <i>m/z</i>	Species		
	PP	PE	dPE
1			H ⁻
2	D ⁻	D ⁻	
13			CH ⁻
25			C ₂ H ⁻
37			C ₃ H ⁻
49			C ₄ H ⁻
50	C ₄ D ⁻	C ₄ D ⁻	

Table S3 N-containing secondary ion species for ND₃ plasma-treated h-PP and h-PE, and NH₃ plasma-treated d-PE samples in their negative ToF-SIMS spectra.

Mass <i>m/z</i>	Species		
	PP	PE	dPE
15	NH ⁻	NH ⁻	NH ⁻
16	NH ₂ ⁻	NH ₂ ⁻	NH ₂ ⁻
17	NH ₃ ⁻ (NHD ⁻)	NH ₃ ⁻ (NHD ⁻)	NH ₃ ⁻ (NHD ⁻)
26	CN ⁻	CN ⁻	CN ⁻
38	C ₂ N ⁻	C ₂ N ⁻	C ₂ N ⁻
39			C ₂ HN ⁻
40		CN ₂ ⁻	CN ₂ ⁻
41		CHN ₂ ⁻	CHN ₂ ⁻

Table S4 O-containing secondary ion species for ND₃ plasma-treated h-PP and h-PE, and NH₃ plasma-treated d-PE samples in their positive ToF-SIMS spectra.

Mass <i>m/z</i>	PP	Species PE	dPE
16		O ⁺	O ⁺
18			H ₂ O ⁺ (OD ⁺)
19	H ₃ O ⁺	H ₃ O ⁺	H ₃ O ⁺
29	CHO ⁺	CHO ⁺	CHO ⁺
30	CDO ⁺ (CH ₂ O ⁺)	CDO ⁺ (CH ₂ O ⁺)	CDO ⁺ (CH ₂ O ⁺)
31	CH ₃ O ⁺ (CDHO ⁺)	CH ₃ O ⁺ (CDHO ⁺)	CH ₃ O ⁺ (CDHO ⁺)
32	CH ₂ DO ⁺ (CD ₂ O ⁺ , CH ₄ O ⁺)	CH ₂ DO ⁺ (CD ₂ O ⁺ , CH ₄ O ⁺)	CD ₂ O ⁺ (CDH ₂ O ⁺ , CH ₄ O ⁺)
33	CHD ₂ O ⁺ (CH ₃ DO ⁺ , CH ₅ O ⁺)	CHD ₂ O ⁺ (CH ₃ DO ⁺ , CH ₅ O ⁺)	CD ₂ HO ⁺ (CH ₃ DO ⁺ , CH ₅ O ⁺)
42	C ₂ DO ⁺ (C ₂ H ₂ O ⁺)	C ₂ DO ⁺ (C ₂ H ₂ O ⁺)	C ₂ H ₂ O ⁺ (C ₂ H ₂ O ⁺)
43	C ₂ H ₃ O ⁺ (C ₂ DHO ⁺)	C ₂ HDO ⁺ (C ₂ H ₃ O ⁺)	C ₂ H ₃ O ⁺ (C ₂ DHO ⁺)
44	CH ₂ NO ⁺ (CDNO ⁺)	CH ₂ NO ⁺ (CDNO ⁺)	CDNO ⁺ (C ₂ H ₂ NO ⁺)
44	C ₂ H ₂ DO ⁺ (C ₂ D ₂ O ⁺ , C ₂ H ₄ O ⁺)	C ₂ H ₂ DO ⁺ (C ₂ D ₂ O ⁺ , C ₂ H ₄ O ⁺)	C ₂ DH ₂ O ⁺ (C ₂ H ₄ O ⁺ , C ₂ D ₂ O ⁺)
45			CH ₃ NO ⁺
45	C ₂ H ₅ O ⁺ (C ₂ H ₃ DO ⁺ , C ₂ HD ₂ O ⁺)	C ₂ H ₅ O ⁺ (C ₂ H ₃ DO ⁺ , C ₂ HD ₂ O ⁺)	C ₂ H ₅ O ⁺ (C ₂ DH ₃ O ⁺ , C ₂ D ₂ HO ⁺)
46	C ₂ H ₂ D ₂ O ⁺ (C ₂ D ₃ O ⁺ , C ₂ H ₄ DO ⁺ , C ₂ H ₆ O ⁺)	C ₂ H ₂ D ₂ O ⁺ (C ₂ D ₃ O ⁺ , C ₂ H ₄ DO ⁺ , C ₂ H ₆ O ⁺)	C ₂ D ₃ O ⁺ (C ₂ D ₂ H ₂ O ⁺ , C ₂ DH ₄ O ⁺)
47			CH ₃ O ₂ ⁺ (CDHO ₂ ⁺)
55	C ₃ H ₃ O ⁺ (C ₃ HDO ⁺)	C ₃ H ₃ O ⁺ (C ₃ HDO ⁺)	C ₃ H ₃ O ⁺ (C ₃ DHO ⁺)
57	C ₃ H ₅ O ⁺ (C ₃ H ₃ DO ⁺ , C ₃ HD ₂ O ⁺)		C ₃ H ₅ O ⁺ (C ₃ DH ₃ O ⁺ , C ₃ D ₂ HO ⁺)
59			C ₃ H ₇ O ⁺ (C ₃ DH ₅ O ⁺ , C ₃ D ₃ H ₃ O ⁺)
60			C ₃ DH ₆ O ⁺ (C ₃ D ₂ H ₄ O ⁺ , C ₃ H ₈ O ⁺ , C ₃ D ₃ H ₂ O ⁺ , C ₃ D ₄ O ⁺)
69	C ₄ H ₅ O ⁺ (C ₄ H ₃ DO ⁺ , C ₄ HD ₂ O ⁺)	C ₄ H ₅ O ⁺ (C ₄ H ₃ DO ⁺ , C ₄ HD ₂ O ⁺)	C ₄ H ₅ O ⁺ (C ₄ DH ₃ O ⁺ , C ₄ D ₂ HO ⁺)

Table S5 O-containing secondary ion species for ND₃ plasma-treated h-PP and h-PE, and NH₃ plasma-treated d-PE samples in their negative ToF-SIMS spectra.

Mass <i>m/z</i>	PP	Species PE	dPE
16	O ⁻	O ⁻	O ⁻
17	OH ⁻	OH ⁻	OH ⁻
18	OD ⁻ (H ₂ O ⁻)	OD ⁻ (H ₂ O ⁻)	OD ⁻ (H ₂ O ⁻)
30	NO ⁻	NO ⁻	NO ⁻
31			CH ₃ O ⁻ (CDHO ⁻)
32	O ₂ ⁻	O ₂ ⁻	O ₂ ⁻
33	O ₂ H ⁻	O ₂ H ⁻	O ₂ H ⁻
42	CNO ⁻	CNO ⁻	CNO ⁻
43	CHNO ⁻	CHNO ⁻	CHNO ⁻
43	C ₂ H ₃ O ⁻ (C ₂ HDO ⁻)	C ₂ H ₃ O ⁻ (C ₂ HDO ⁻)	C ₂ H ₃ O ⁻ (C ₂ HDO ⁻)
45	CHO ₂ ⁻	CHO ₂ ⁻	CHO ₂ ⁻