Supplementary Information

Pyrolysis-gas chromatography/mass spectrometry conditions

Table S1

Pyrolytic Conditions.

Pyrolysis Conditions	
Instrument	CDS 6200 pyroprobe pyrolysis unit with DISC inlet
Trap	Tenax-TA
Carrier gas	Helium
Pyrolysis temperature	610 °C
Pyrolysis time	20 s
Transfer line temperature	310 °C
Gas Chromatography Conditions	
Instrument	ThermoScientific Trace 1310 GC
Injector Mode	Split 20:1
Injector temperature	310 °C
Column	HP-1 fused, 60 m × 0.32 mm i.d. × 0.25 μm film thickness
Flow	2 mL min^{-1}
Temperature programme	40 °C (4 min) → 300 °C (15 min)
Mass Spectrometry Conditions	
Instrument	ThermoScientific single quadrupole MS
Ionisation energy	70 eV
Scan speed	5 scans s^{-1}
Scan range	50–650

Chromatograms of each plastic standard, with and without thermochemolysis

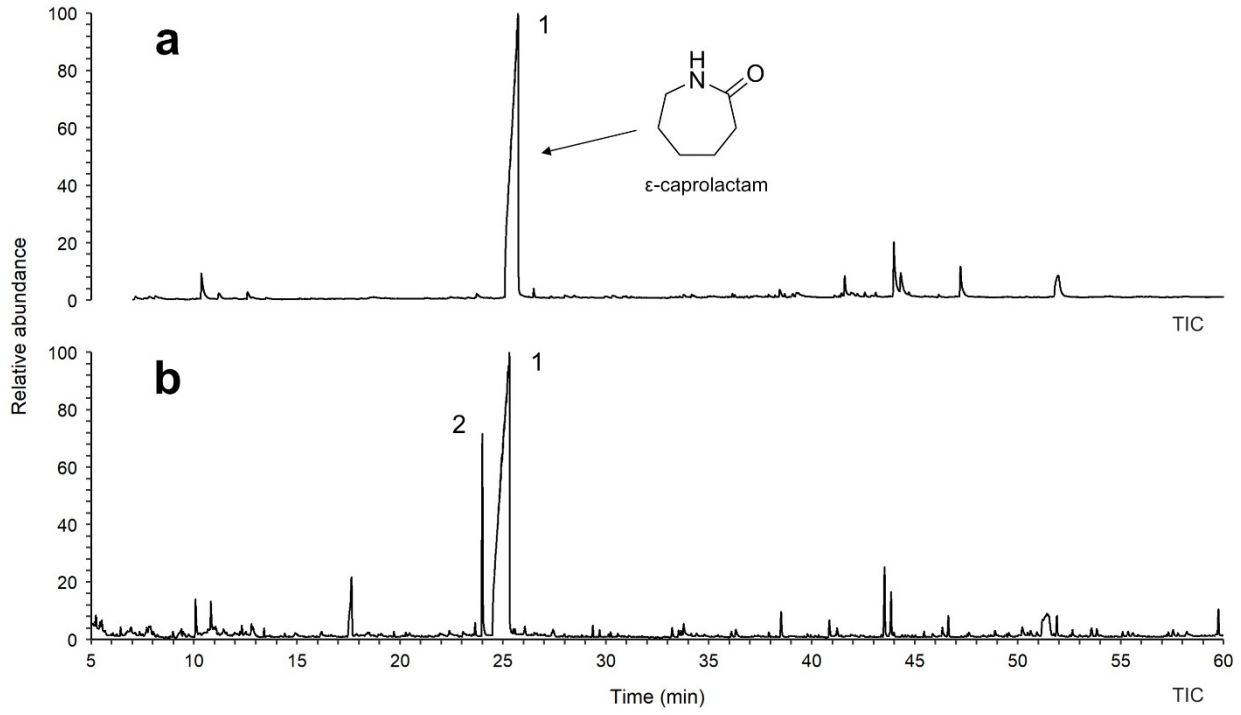

Figure S1. Py-GC/MS chromatograms of PA6 (a) without thermochemolysis and (b) with thermochemolysis. See Table S2 for peak identification.

Table S2

Characteristic pyrolytic products of PA6, with their respective labels.

Peak	Compound	Peak	Compound
1*	ε-caprolactam	**2†**	*N*-methyl caprolactam

* = selected diagnostic compounds
† = thermochemolytic product

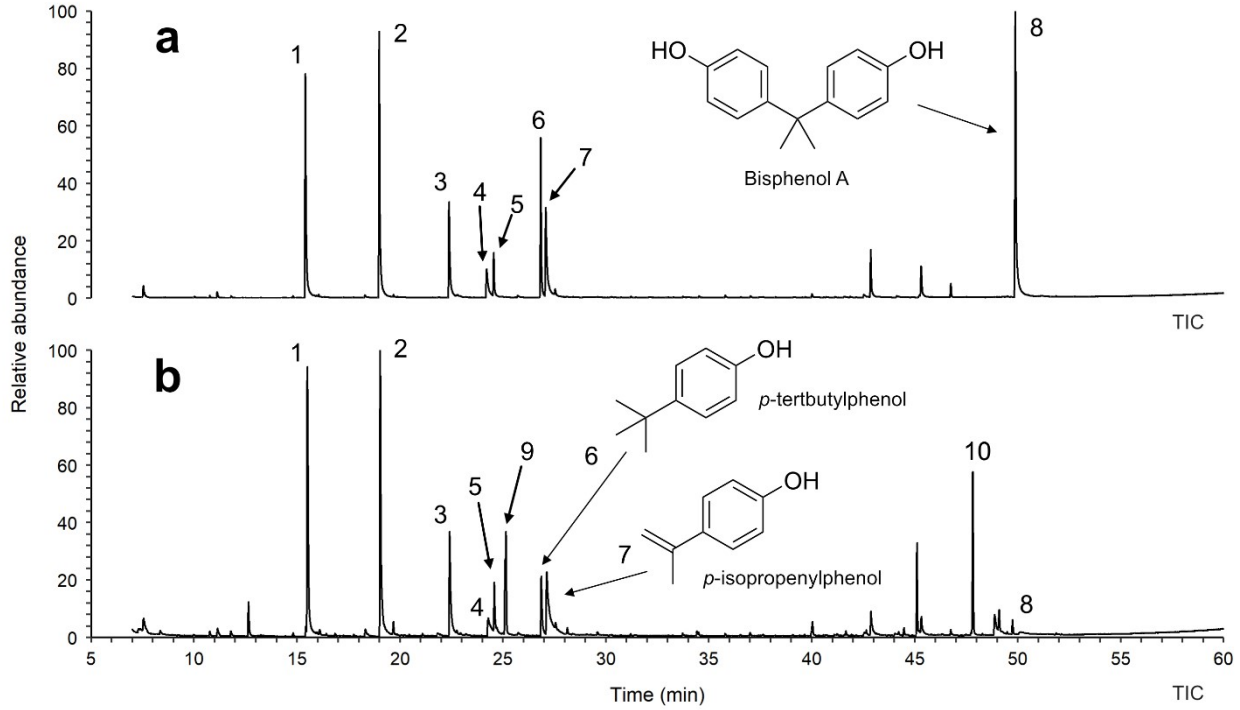

Figure S2. Py-GC/MS chromatograms of PC (a) without thermochemolysis and (b) with thermochemolysis. See Table S3 for peak identification.

Table S3

Characteristic pyrolytic products of PC, with their respective labels.

Peak	Compound
1	Phenol
2	*p*-cresol
3	*p*-ethylphenol
4	*p*-vinylphenol
5	*p*-isopropylphenol
6*	*p*-tertbutylphenol
7*	*p*-isopropenylphenol
8*	Bisphenol A
9†	*p*-methoxy-tert-butylbenzene
10†	2,2-Bis(4'-methoxyphenyl)propane

* = selected diagnostic compounds

† = thermochemolytic product

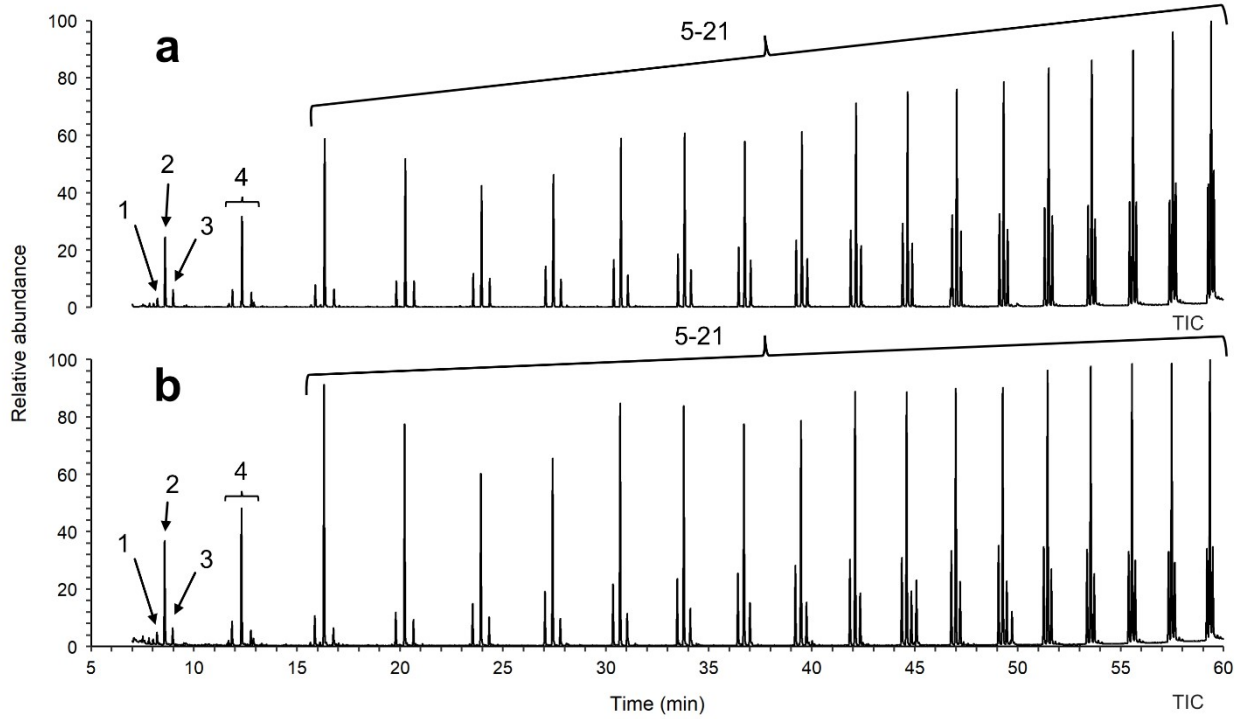

Figure S3. Py-GC/MS chromatograms of PE (a) without thermochemolysis and (b) with thermochemolysis. See Table S4 for peak identification.

Table S4

Characteristic pyrolytic products of PE, with their respective labels.

Peak	Compound	Peak	Compound
1	Octa-1,7-diene	**3**	Octane
2	Oct-1-ene	**4**	Non-1-ene

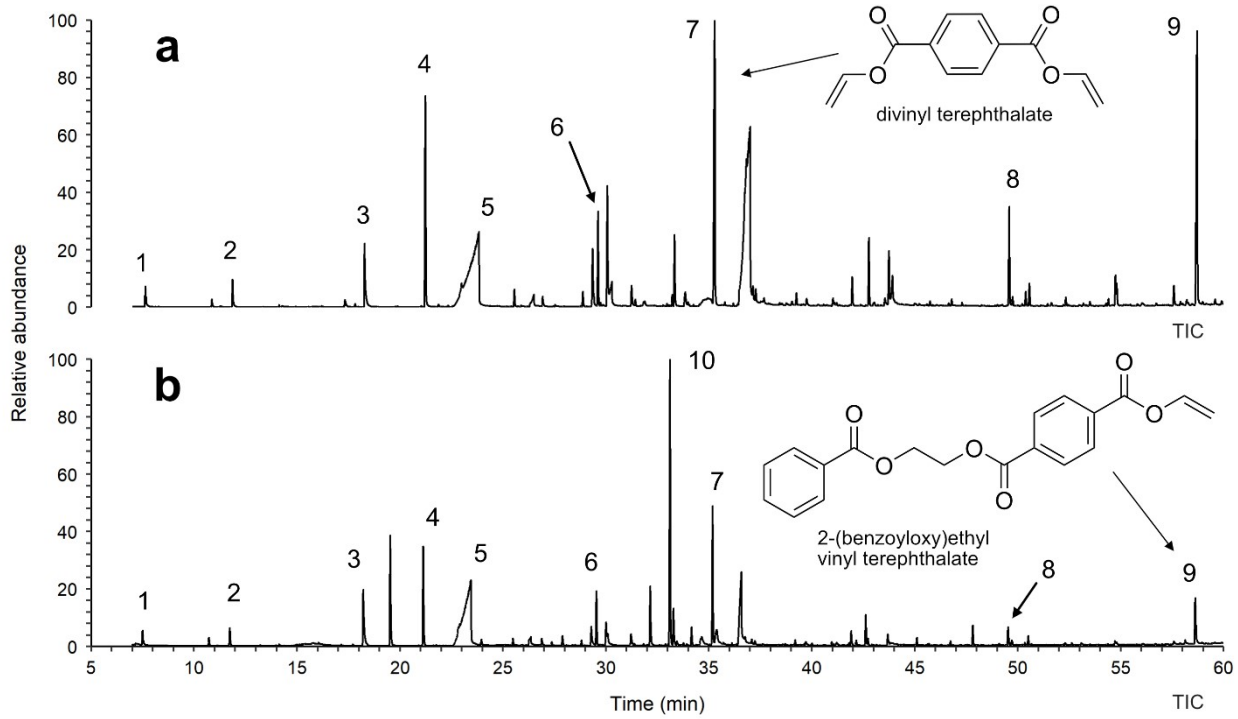

Figure S4. Py-GC/MS chromatograms of PET (a) without thermochemolysis and (b) with thermochemolysis. See Table S5 for peak identification.

Table S5

Characteristic pyrolytic products of PET, with their respective labels.

Peak	Compound
1	Toluene
2	Styrene
3	Acetophenone
4	Vinyl benzoate
5	Benzoic acid
6	Biphenyl
7*	Divinyl terephthalate
8	Ethane-1,2-diyldibenzoate
9*	2-(benzoyloxy)ethyl vinyl terephthalate
10†	Dimethyl terephthalate

* = selected diagnostic compounds
† = thermochemolytic product

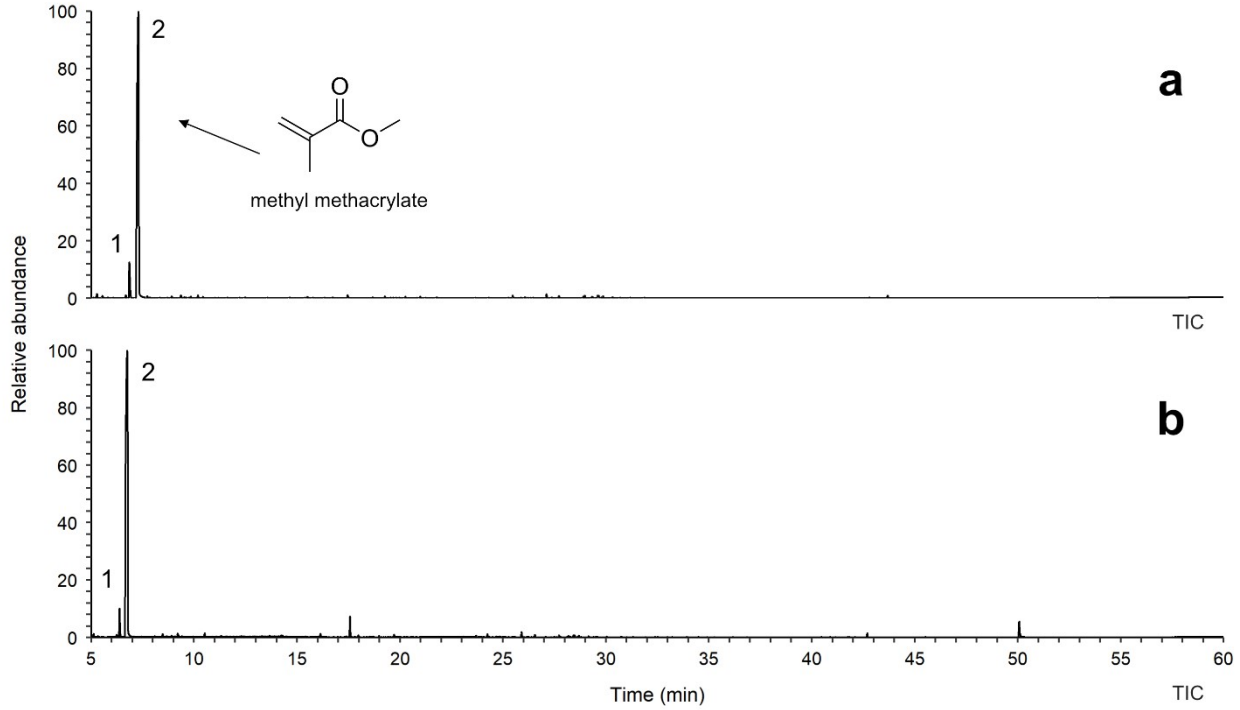

Figure S5. Py-GC/MS chromatograms of PMMA (a) without thermochemolysis and (b) with thermochemolysis. See Table S6 for peak identification.

Table S6

Characteristic pyrolytic products of PMMA, with their respective labels.

Peak	Compound
1	Methyl acrylate
2*	Methyl methacrylate

* = selected diagnostic compounds

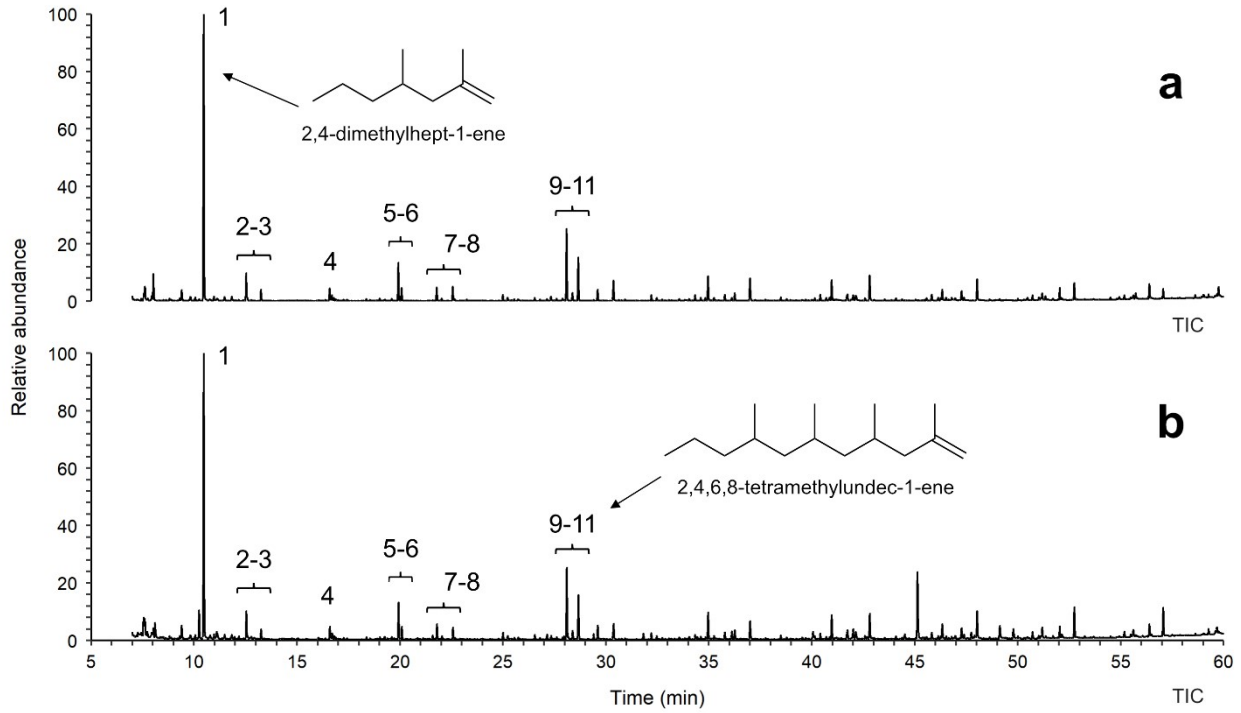

Figure S6. Py-GC/MS chromatograms of PP (a) without thermochemolysis and (b) with thermochemolysis. See Table S7 for peak identification.

Table S7

Characteristic pyrolytic products of PP, with their respective labels.

Peak	Compound
1*	2,4-dimethylhept-1-ene
2-3	2,4,6-trimethylhepta-1,6-diene, 2,4,6-trimethylhept-1-ene
4	4,6-dimethylnon-2-ene
5-6	2,4,6-trimethylnon-1-ene (meso and racemic)
7-8	2,4,6,8-tetramethylnona-1,8-diene, 2,4,6,8-tetramethylnon-1-ene
9-11*	2,4,6,8-tetramethylundec-1-ene (isotactic, heterotactic and syndiotactic)

* = selected diagnostic compounds

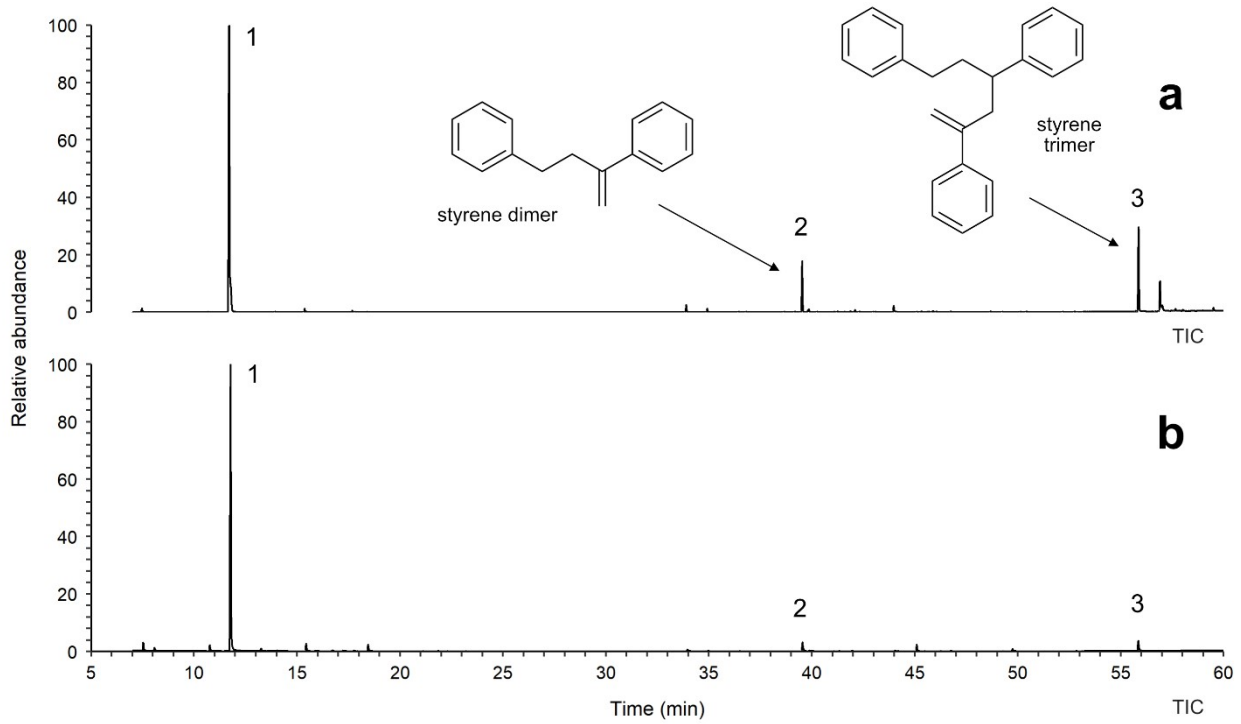

Figure S7. Py-GC/MS chromatograms of PS (a) without thermochemolysis and (b) with thermochemolysis. See Table S8 for peak identification.

Table S8

Characteristic pyrolytic products of PS, with their respective labels.

Peak	Compound
1	Styrene
2*	But-3-ene-1,3-diyldibenzene (styrene dimer)
3*	Hex-5-ene-1,3,5-triyltribenzene (styrene trimer)

* = selected diagnostic compounds

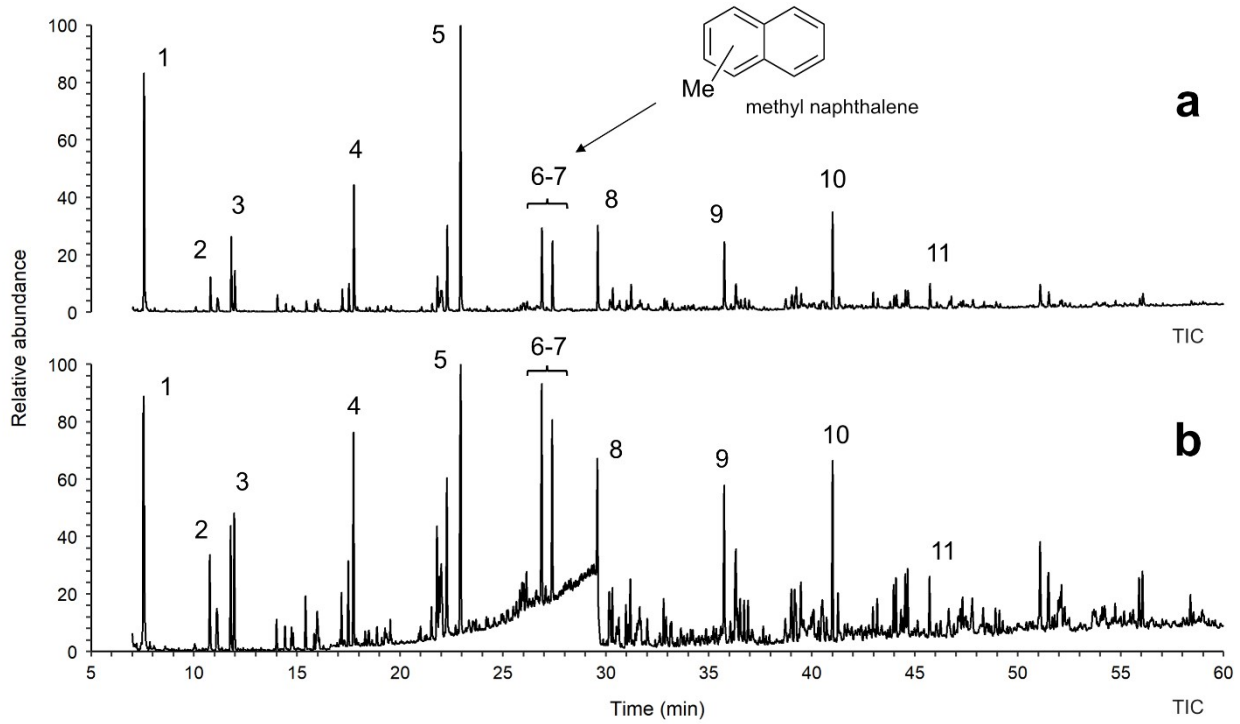

Figure S8. Py-GC/MS chromatograms of PVC (a) without thermochemolysis and (b) with thermochemolysis. See Table S9 for peak identification.

Table S9

Characteristic pyrolytic products of PVC, with their respective labels.

Peak	Compound
1	Toluene
2	Ethylbenzene
3	Styrene
4	Indene
5	Naphthalene

Peak	Compound
6-7*	Methyl naphthalenes
8	Biphenyl
9	Fluorene
10	Anthracene
11	Pyrene

* = selected diagnostic compounds

Filtered chromatograms and mass spectra for each plastic standard and selected diagnostic compounds

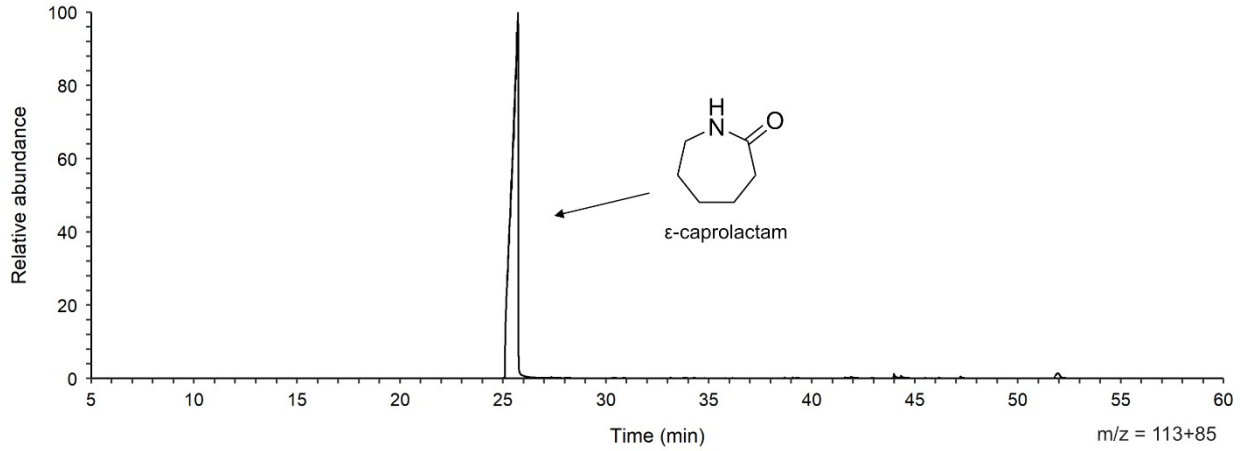

Figure S9. Py-GC/MS chromatogram of PA6 filtered by *m/z* 113+85.

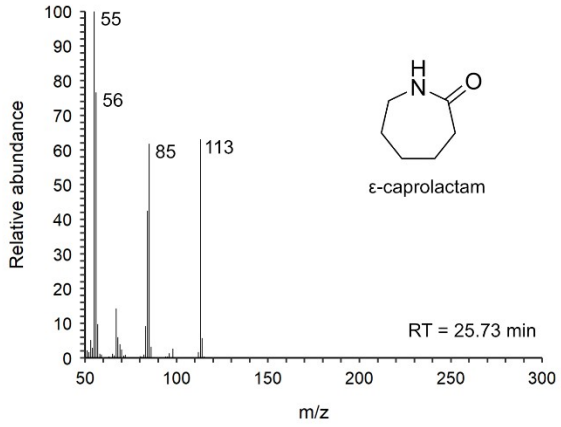

Figure S10. Mass spectrum of ε-caprolactam taken from the pyrogram of PA6 above.

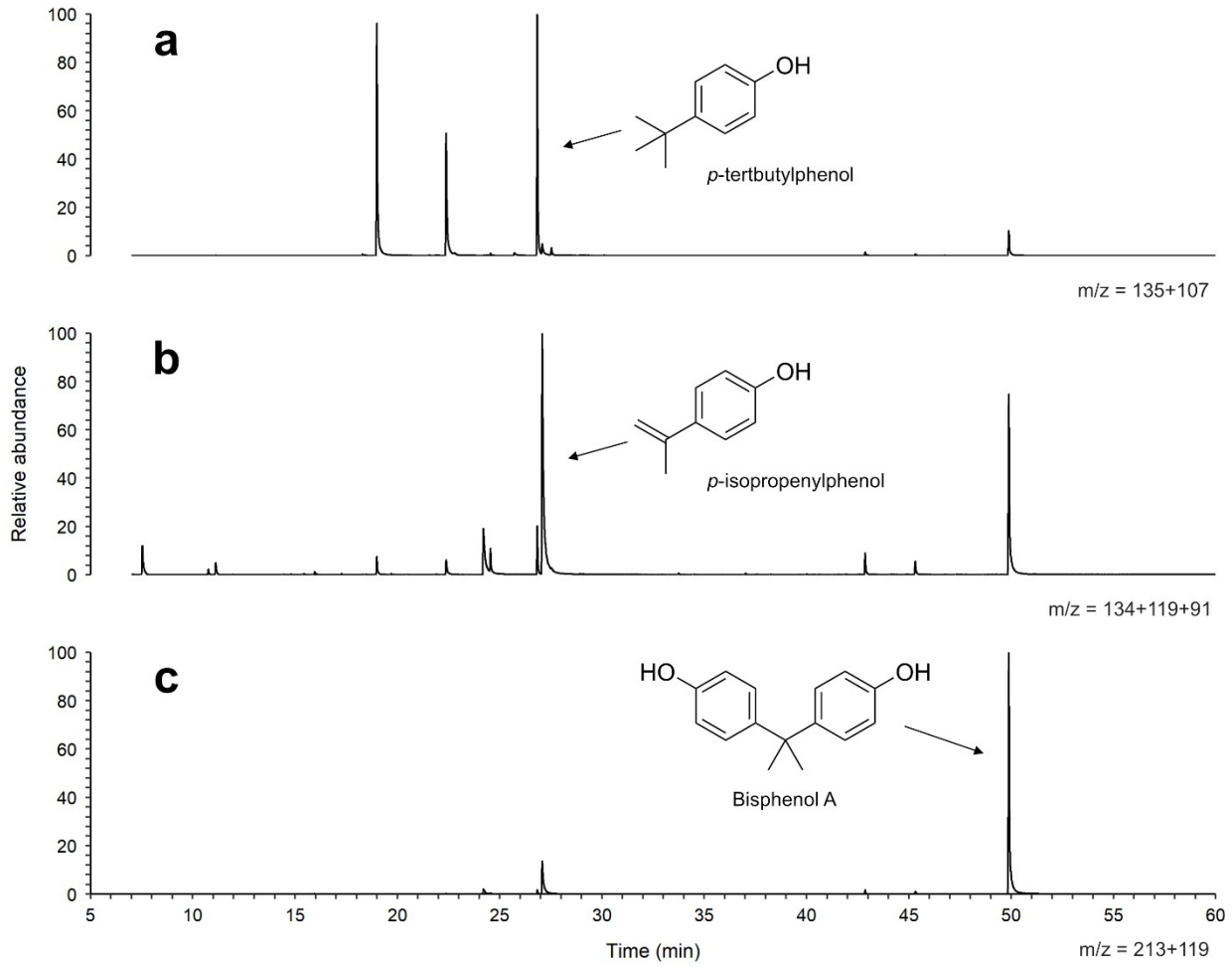

Figure S11. Py-GC/MS chromatograms of PC filtered by *m/z* (a) 135+107, (b) 134+119+91 and (c) 213+119.

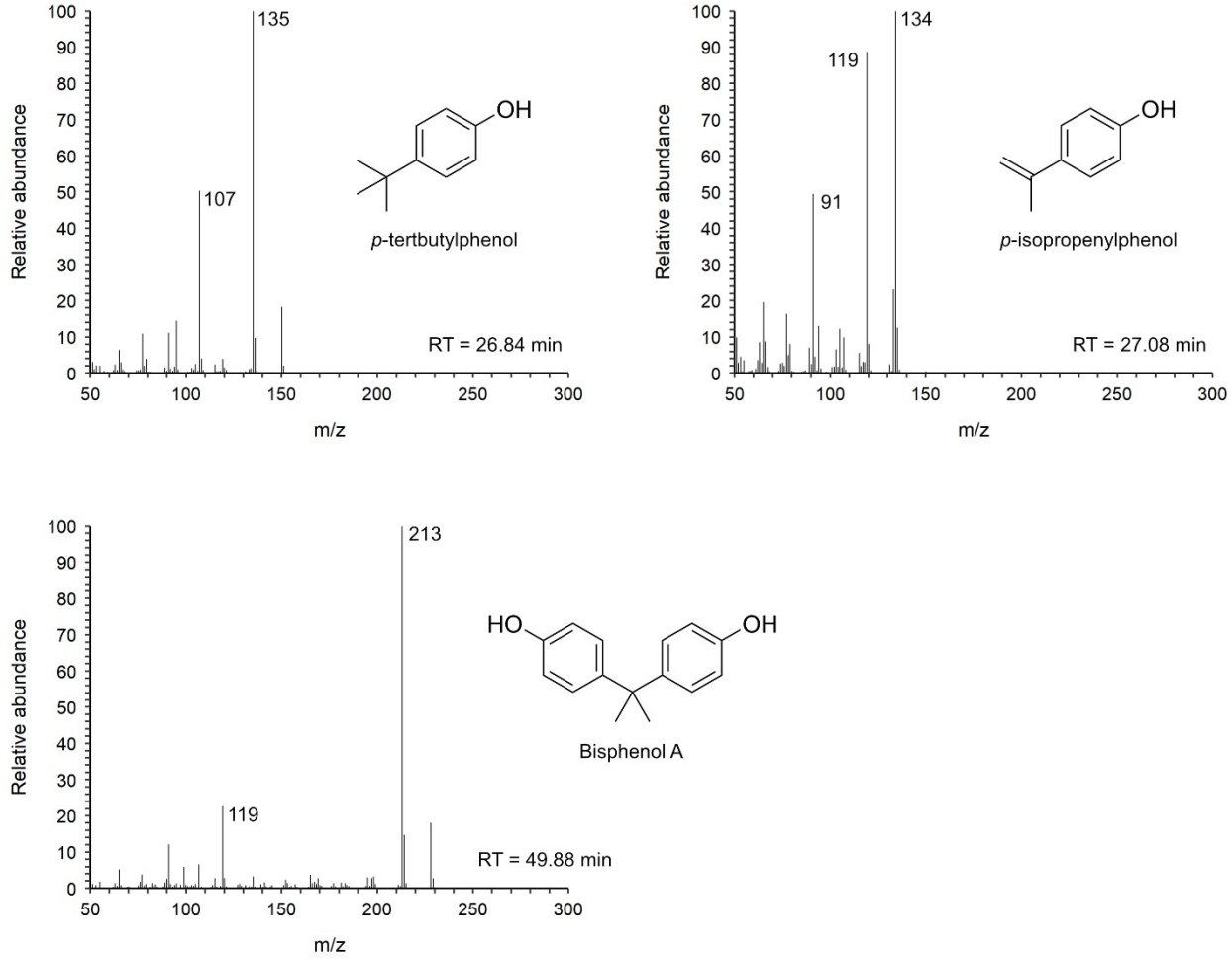

Figure S12. Mass spectra of (a) *p*-tertbutylphenol, (b) *p*-isopropenylphenol and (c) bisphenol A taken from the pyrogram of PC above.

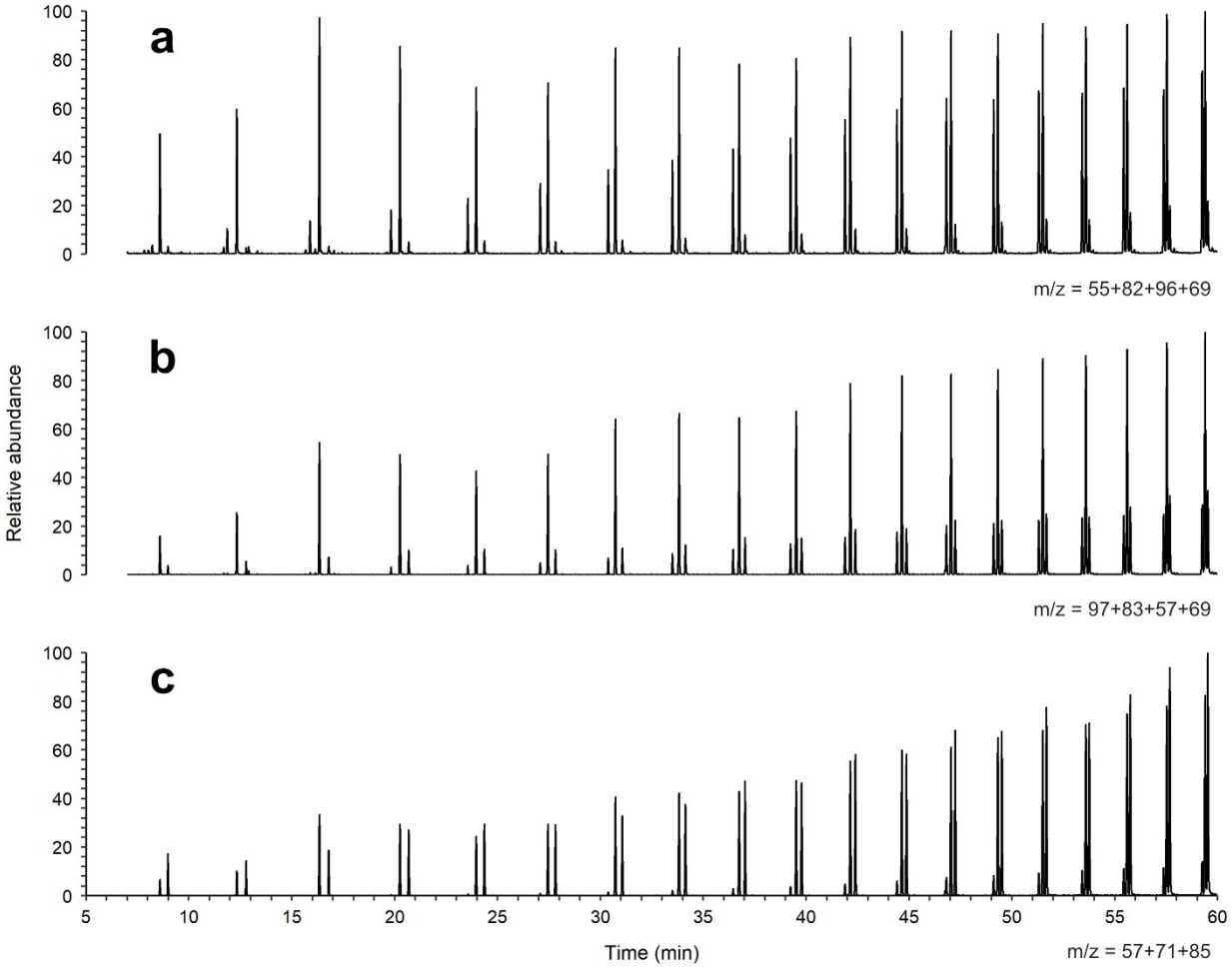

Figure S13. Py-GC/MS chromatograms of PE filtered by *m/z* (a) 55+82+96+69, (b) 97+83+57+69 and (c) 57+71+85.

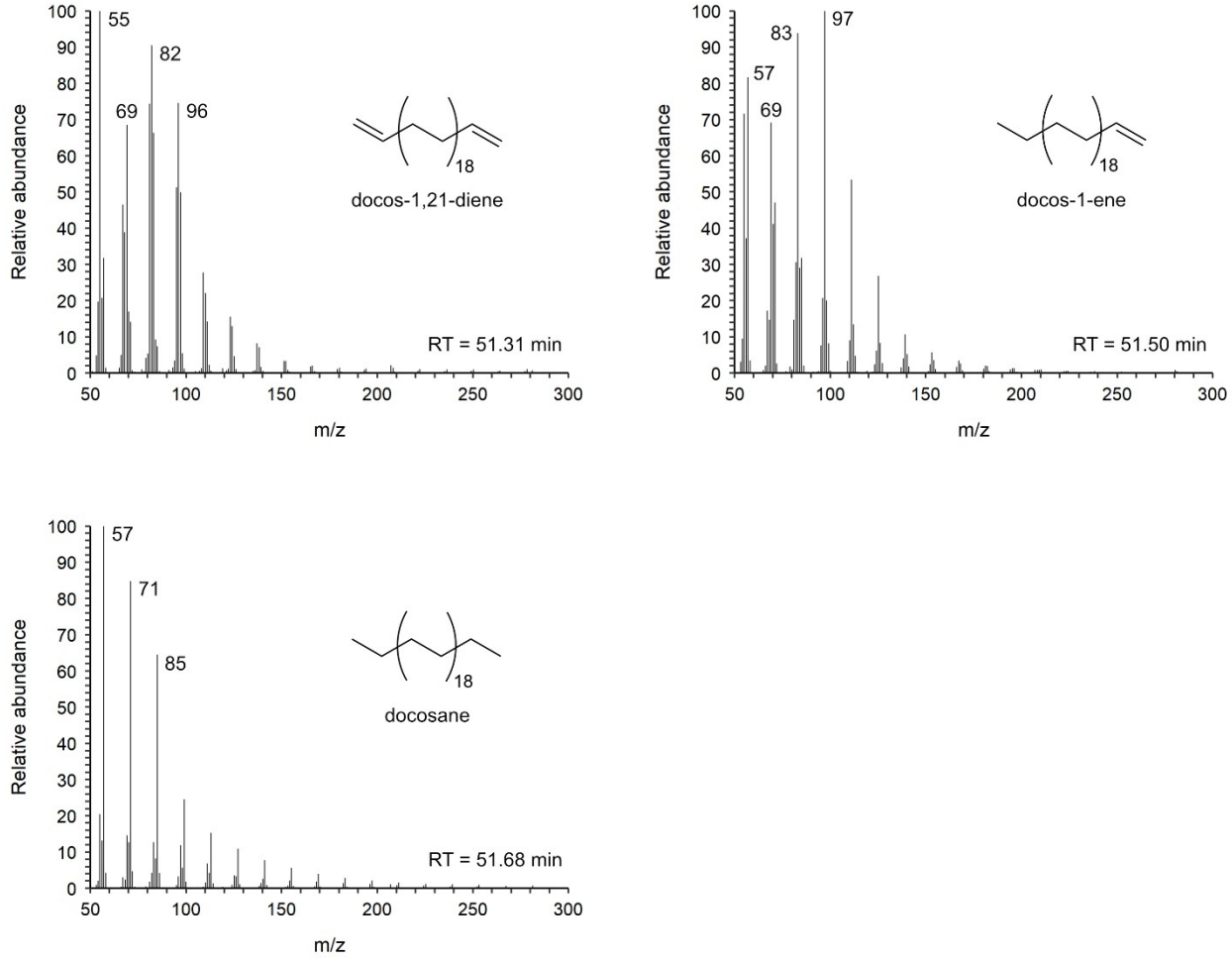

Figure S14. Mass spectra of (a) docosa-1,21-diene, (b) docos-1-ene and (c) docosane taken from the pyrogram of PE above.

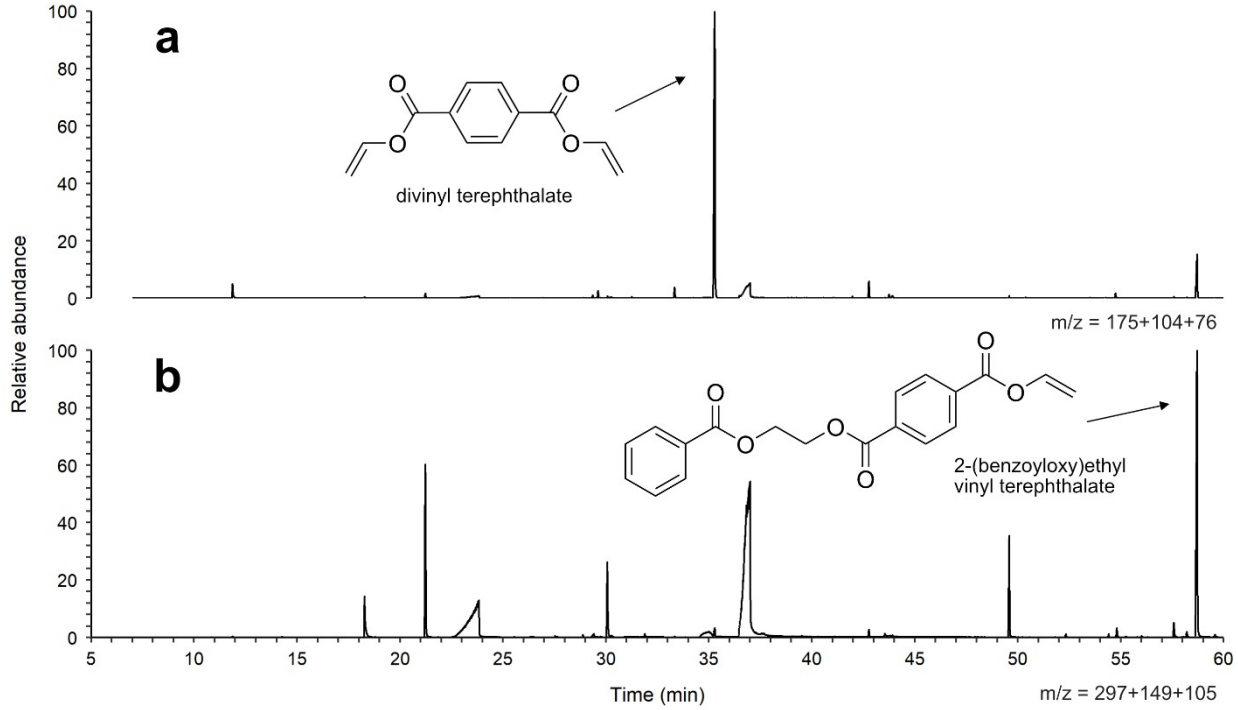

Figure S15. Py-GC/MS chromatograms of PET filtered by *m/z* (a) 175+104+76 and (b) 297+149+105.

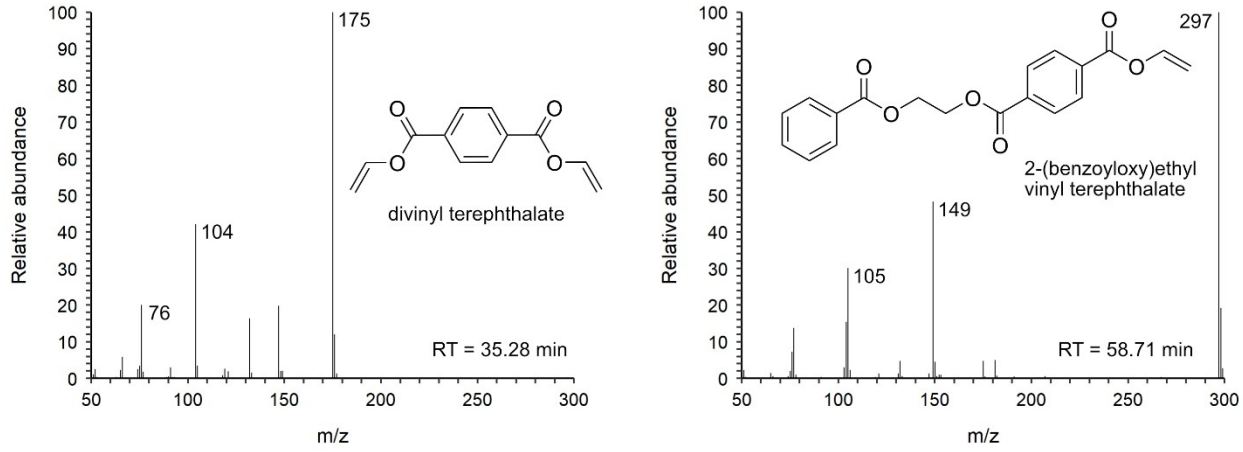

Figure S16. Mass spectra of (a) divinyl terephthalate and (b) 2-(benzoyloxy)ethyl vinyl terephthalate taken from the pyrogram of PET above.

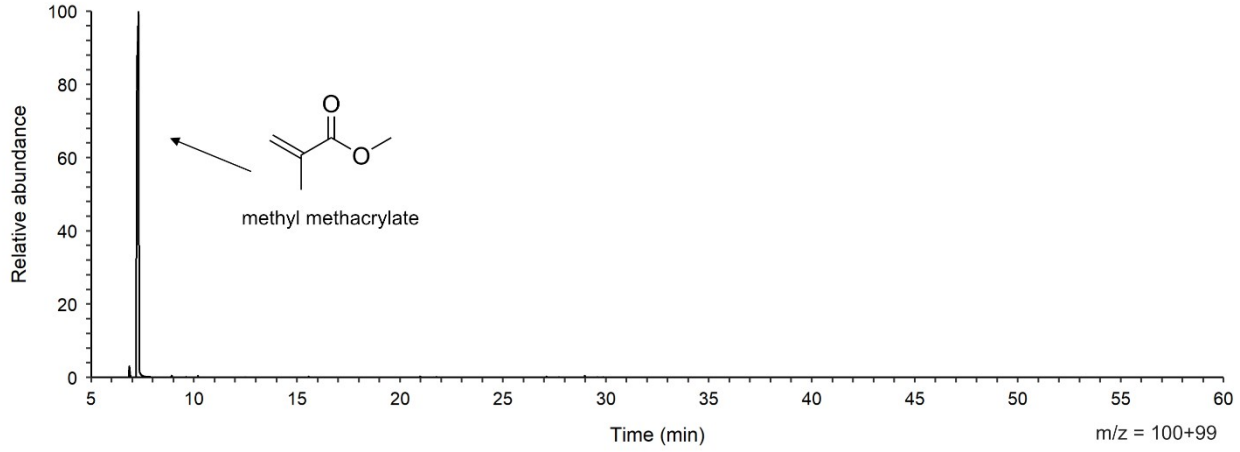

Figure S17. Py-GC/MS chromatogram of PMMA filtered by *m/z* 100+99.

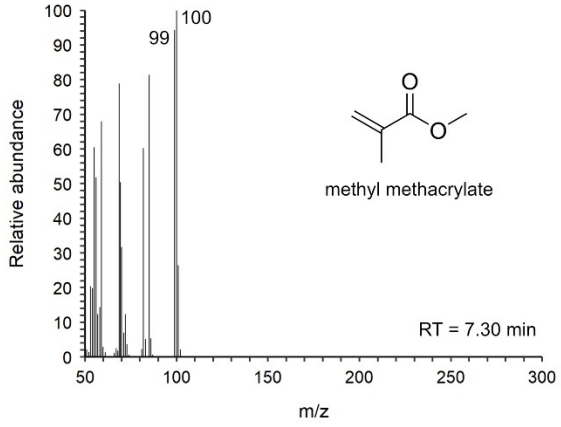

Figure S18. Mass spectrum of methyl methacrylate taken from the pyrogram of PMMA above.

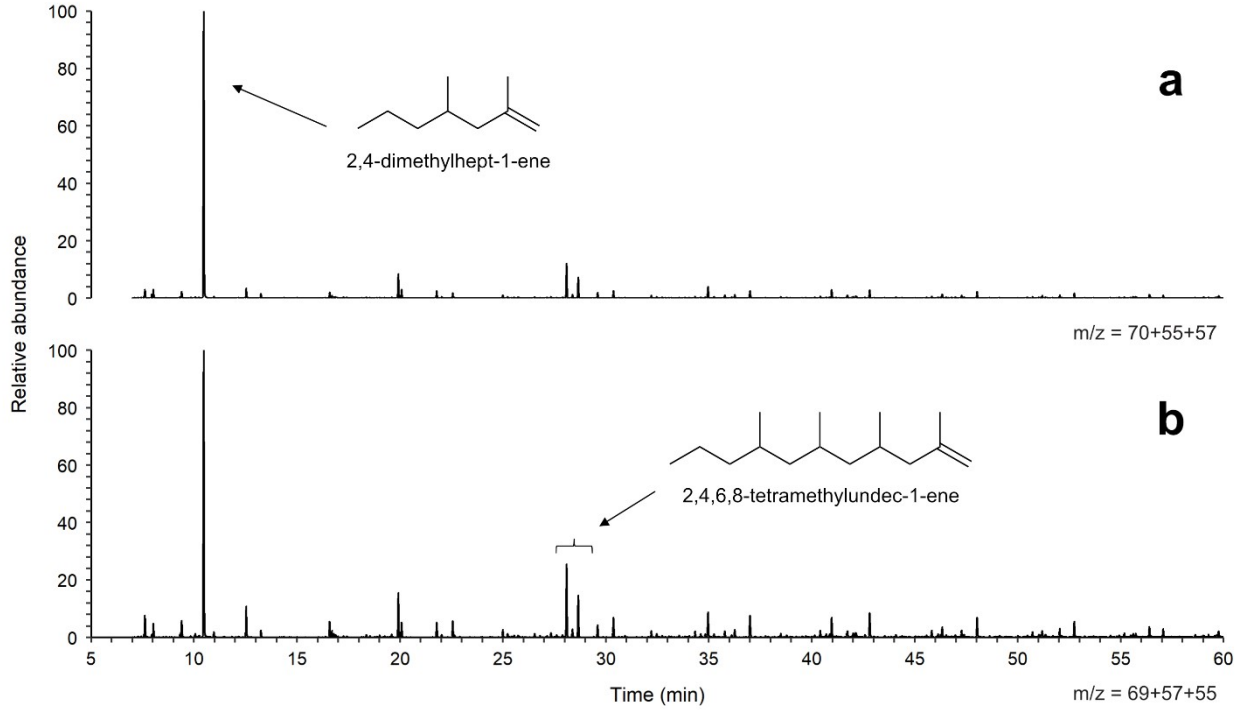

Figure S19. Py-GC/MS chromatograms of PP filtered by *m/z* (a) 70+55+57 and (b) 69+57+55.

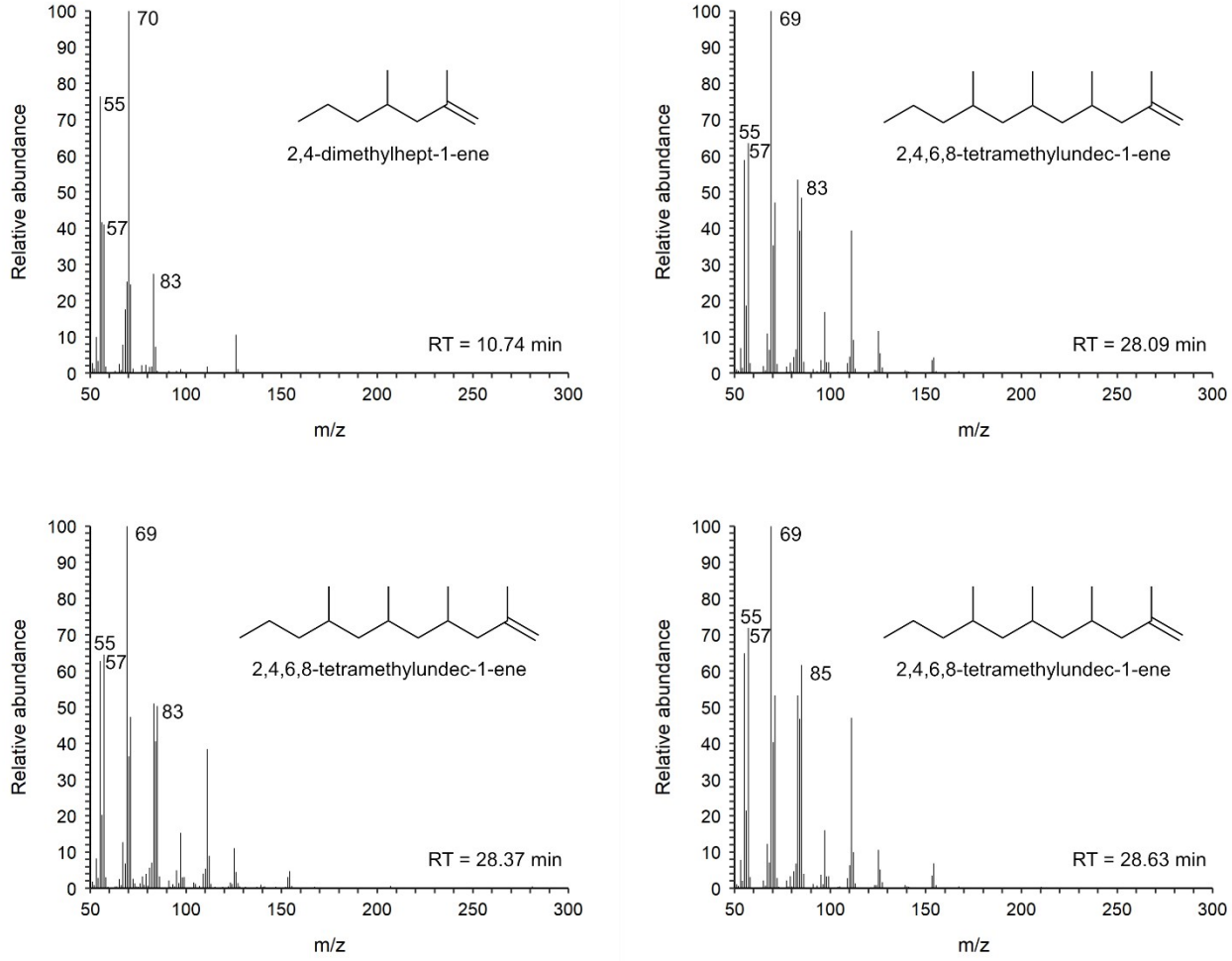

Figure S20. Mass spectra of (a) 2,4-dimethylhept-1-ene and (b-d) 2,4,6,8-tetramethylundec-1-ene (isotactic, heterotactic and syndiotactic isomers) taken from the pyrogram of PP above.

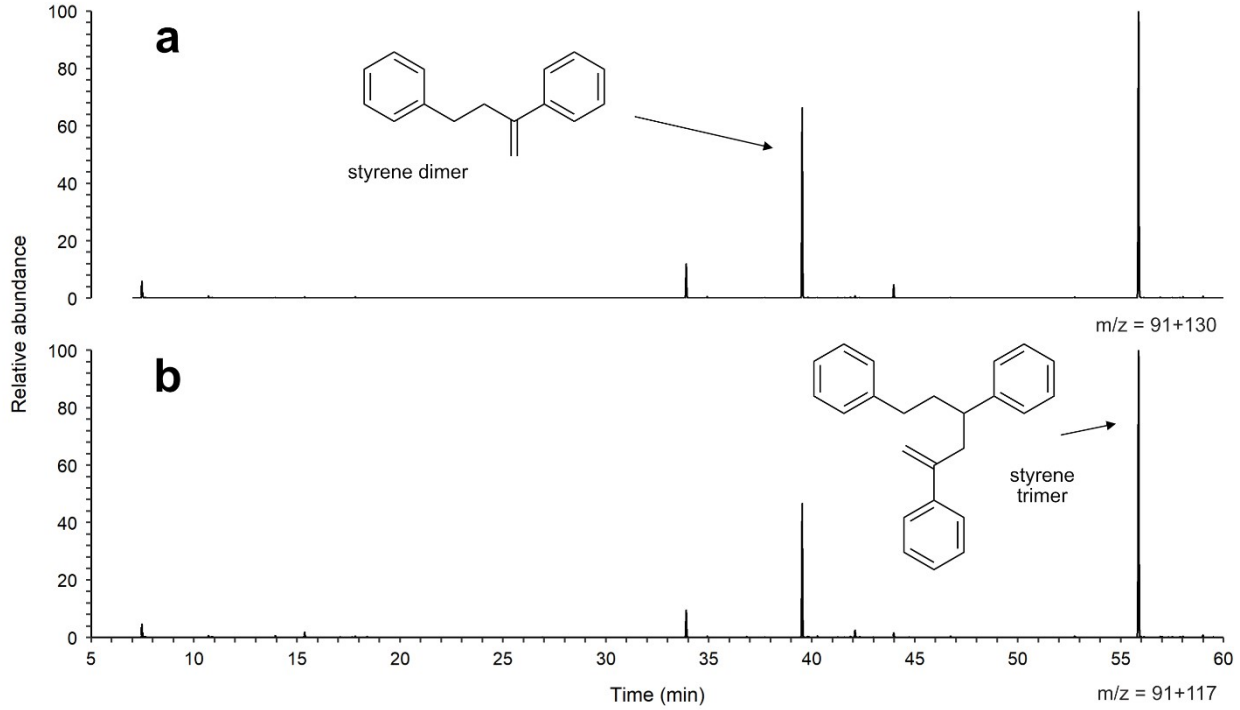

Figure S21. Py-GC/MS chromatograms of PS filtered by *m/z* (a) 91+130 and (b) 91+117.

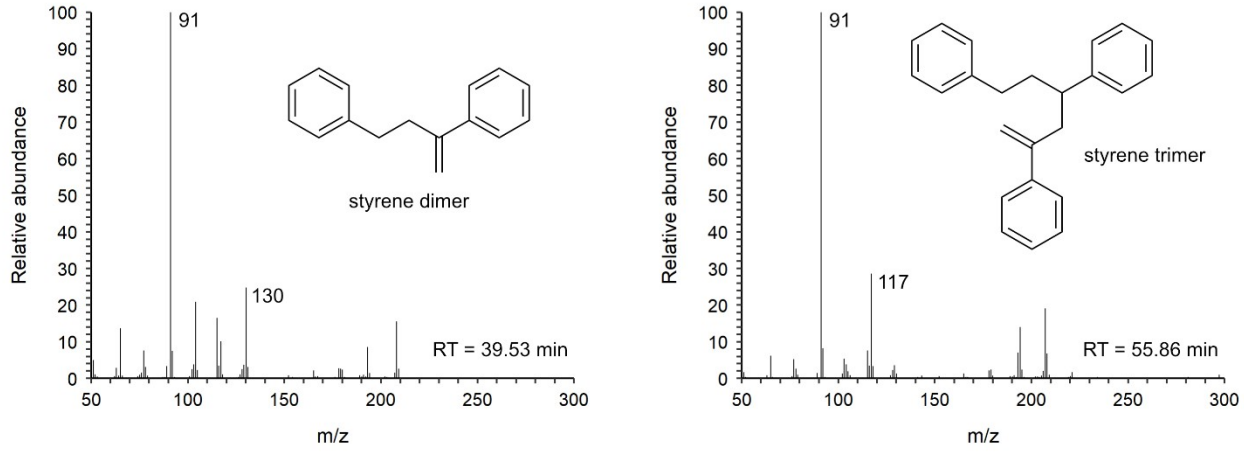

Figure S22. Mass spectra of (a) but-3-ene-1,3-diyldibenzene and (b) hex-5-ene-1,3,5-triyltribenzene taken from the pyrogram of PS above.

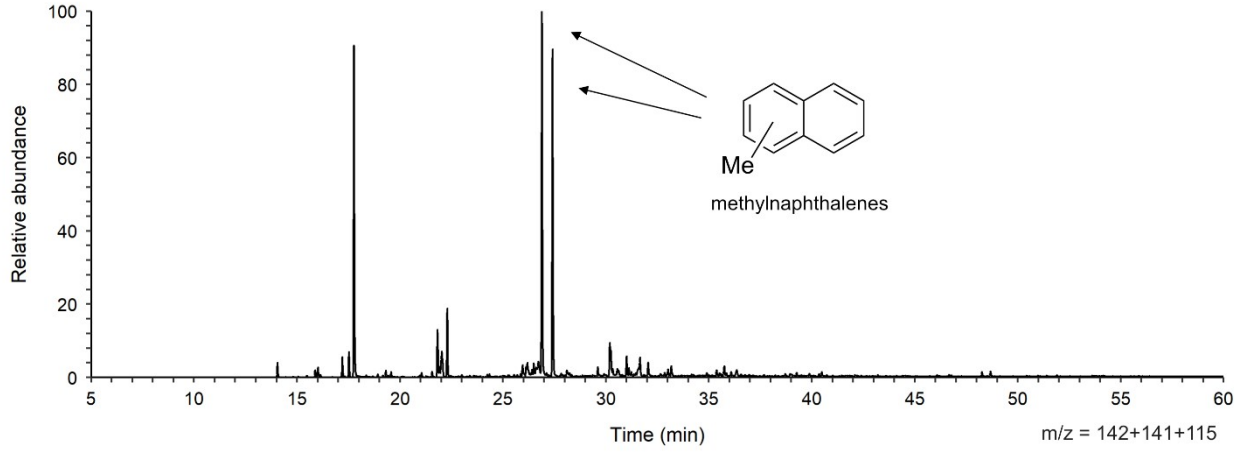

Figure S23. Py-GC/MS chromatogram of PVC filtered by *m/z* 142+141+115.

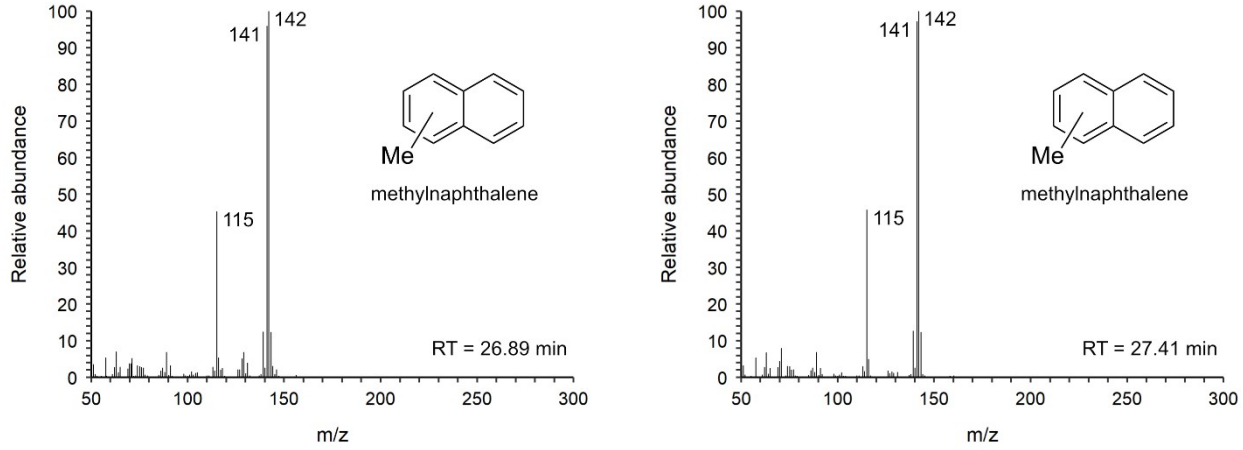

Figure S24. Mass spectra of the two methylnaphthalene isomers taken from the pyrogram of PVC above.

Recovery of each plastic standard using different extraction methods

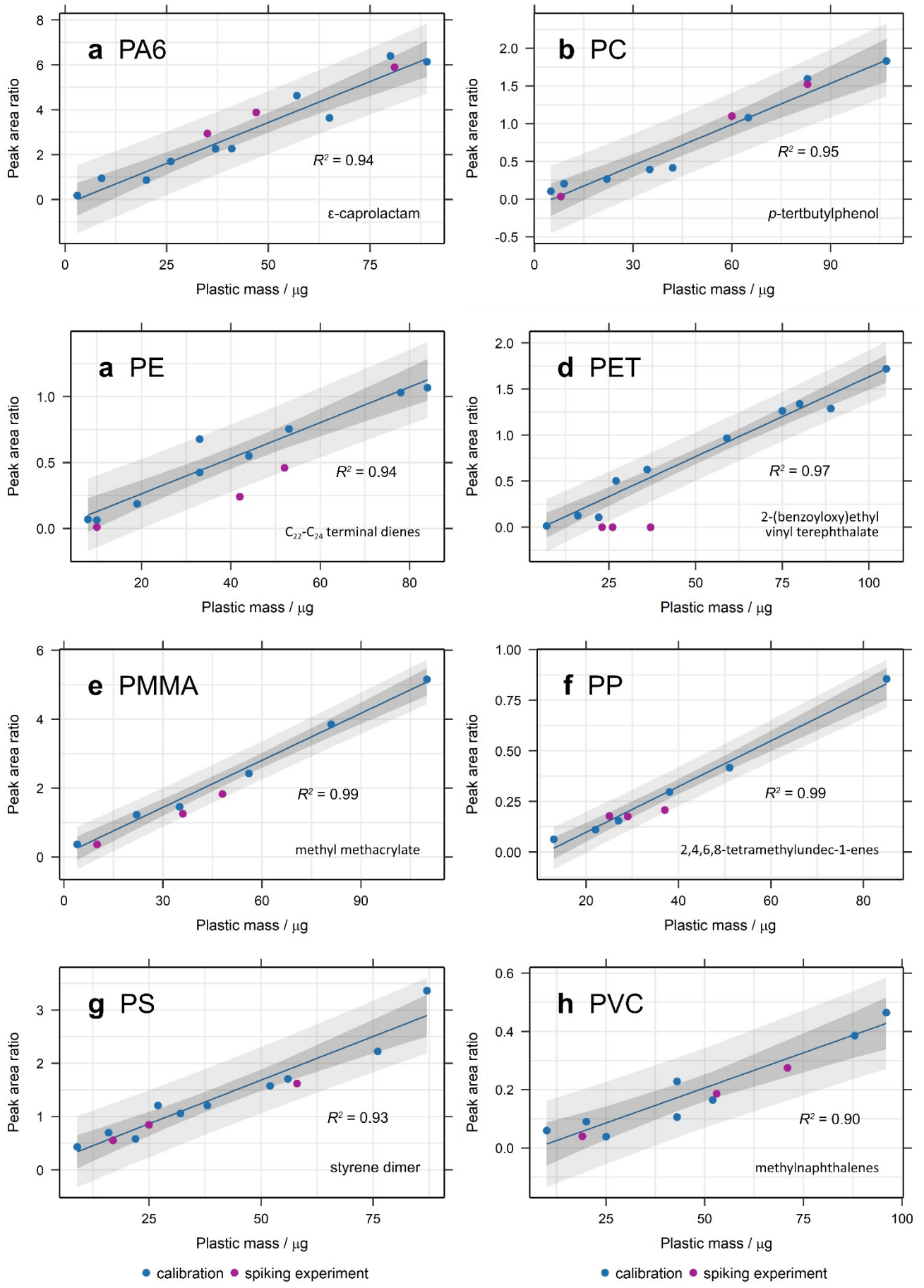

Figure S25. Recovery of (a) PA6, (b) PC, (c) PE, (d) PET, (e) PMMA, (f) PP, (g) PS and (h) PVC from spiked sand after density separation *via* overnight settling. Calibration curves were created from the ion chromatogram

peak area ratio of each selected diagnostic compound with anthracene-d_{10} or pyrene-d_{10} as the internal standard and 95% confidence and prediction bands plotted.

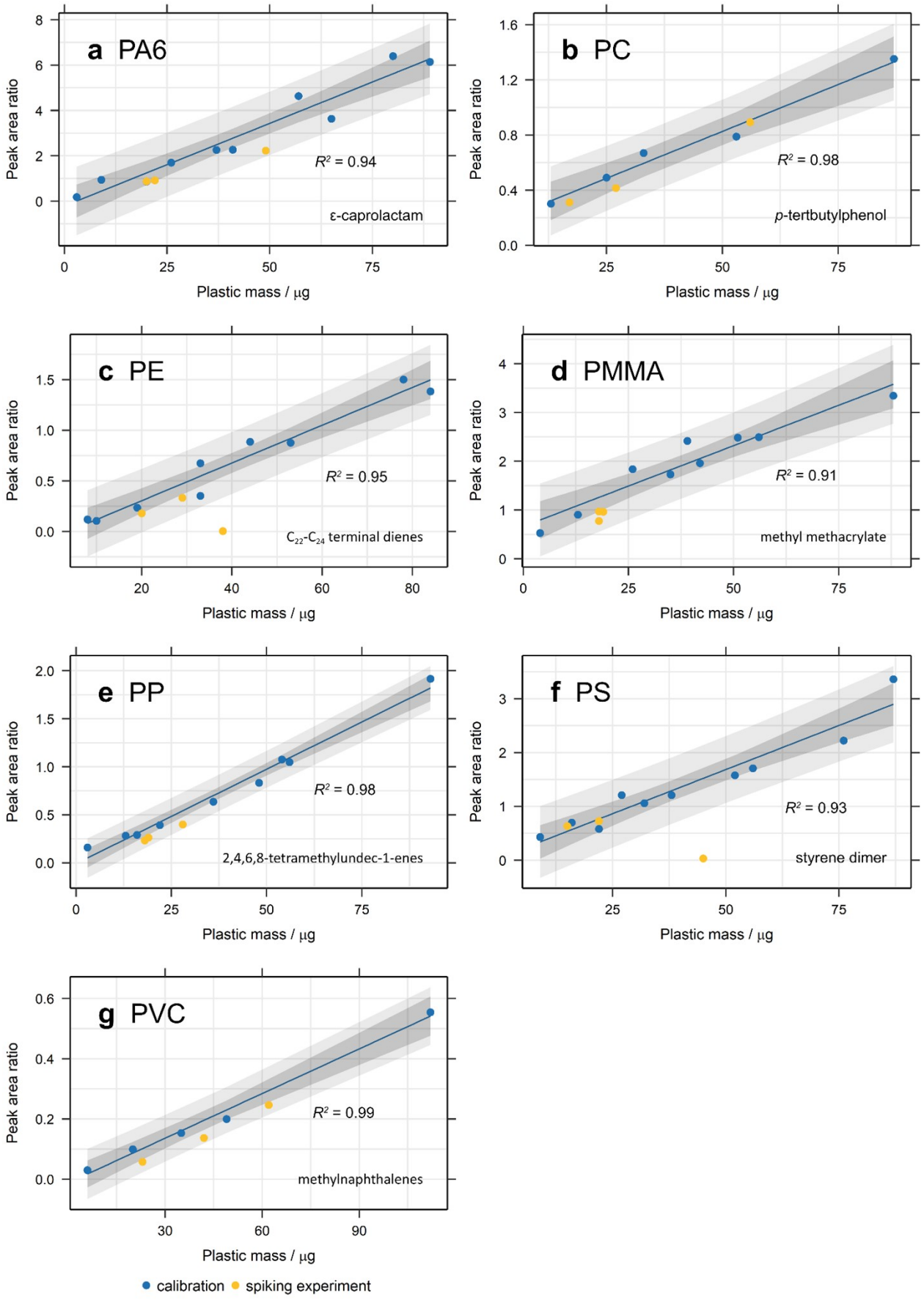

Figure S26. Recovery of (a) PA6, (b) PC, (c) PE, (d) PMMA, (e) PP, (f) PS and (g) PVC from spiked soil samples after density separation *via* overnight settling and hydrogen peroxide digestion in a filter holder. Calibration curves were created from the ion chromatogram peak area ratio of each selected diagnostic

compound with anthracene-d_{10} or pyrene-d_{10} as the internal standard and 95% confidence and prediction bands plotted.