Supplementary Information (SI) for Materials Horizons.

Supplementary Information

Highly adaptable oxidative upcycling of polyolefins to multifunctional chemicals containing·oxygen and nitrogen

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Materials

PP pellets were purchased from China National Petroleum Corporation. LDPE, LLDPE, HDPE and POE powders were purchased from Macklin. Terephthalaldehyde and thiourea dioxide were purchased from adamas-beta. Concentrated nitric acid and concentrated sulfuric acid were purchased from Chron Chemicals. Potassium hydroxide, sodium hydroxide and tetrahydrofuran were purchased from Tianjin aopusheng Chemical Co., Ltd.

Methods

Oxidative Degradation of PP

The 0.8 g LDPE powder and 5 mL of 4 M HNO3 were added to a 50 mL hydrothermal reactor with a PTFE stirrer. The reactor was sealed and placed in a 140 oC oil bath with stirring for 2 h. At the end of the reaction, the reactor was cooled to room temperature with cold water. After opening the reactor, the liquid was decanted out and methylene chloride was used to dissolve the solids adhering to the liner wall. The DCM was removed by rotary evaporation to give the oxidative degradation product DLDPE.

The mass yields of the degradation products were calculated according to Eq. S1.

$$\text{Yield (wt\%)} = \frac{W_{DLDPE}}{W_{LDPE}} \times 100\% \qquad \text{Eq. S1}$$

Where WLDPE and WDLDPE is the mass of LDPE and DLDPE, respectively.

Functional group contents

A 10 g/L phenolphthalein ethanol solution and a 0.1 mol/L KOH ethanol standard solution were prepared. Blank titration: 20 mL of THF was added to a 250 mL Erlenmeyer flask. Add 2~3 drops of phenolphthalein solution as an indicator. The titration was performed with KOH standard solution, and the appearance of a persistent pink color that did not fade for 30 s was considered as the endpoint of the titration. Then, the volume of KOH standard solution consumed was recorded. Sample titration: 100 mg of DLDPE was weighed and dissolved in 20 mL of THF. 2~3 drops of phenolphthalein solution were added to the sample solution. The sample solution was titrated with KOH solution until the solution turned pink and kept the color for 30 s without fading. The volume of KOH solution consumed was recorded as V_{DLDPE}, and the carboxylic acid content in DLDPE was calculated after deducting the blank volume V_{blank}. The content of carboxyl group in the degradation products was calculated according to Eq. S2

$$a_{COOH}\,(mmol/g) = \frac{(V_{DLDPE} - V_{blank}) \times 10^{-3} \times C_{KOH} \times 10^{3}}{W_{DLDPE} \times 10^{-3}} \quad \text{Eq. S2}$$

Where a_{COOH} is the content of carboxyl group, and C_{KOH} is the concentration of KOH solution.

The content of nitro group in the degradation products was calculated according to Eq. S3. Where A_{NO2} and A_{COOH} are the maximum absorbance of the infrared absorption peak of the nitro group at 1550 cm^{-1} and carboxyl group at 1714 cm^{-1} respectively; ε_{COOH} and ε_{NO2} is the molar absorption coefficient of carboxyl and nitro respectively and their ratio was taken as 1.

$$a_{NO_2}(\mathrm{mmol/g}) = \frac{A_{NO_2}}{A_{COOH}} \times \frac{\varepsilon_{COOH}}{\varepsilon_{NO_2}} \times a_{COOH} \quad \text{Eq. S3}$$

In-situ EPR experiments

An in situ and integrated reaction and detection setup was built on an electron paramagnetic resonance spectrometer (Bruker A300, Germany). In a typical reaction, 100 μL of reaction solution was taken at 20 min, 40 min and 90 min, and then 5 μL of DMPO was added to the solution as a trapping agent and tested.

High-value application of degradation products

Surfactant: DLDPE was dissolved in THF, and sodium hydroxide solution was added slowly and dropwise until the solid was completely dissolved. The solvent was removed by rotary evaporation to obtain DLDPE sodium salt. Add dichloromethane to the aqueous solution of DLDPE sodium salt, and the stability of the emulsion was observed after repeated oscillations. The mixed solution of DCM and water was used as the control group, and its stability was also observed after oscillation.

pH buffer: 0.01 M NaOH solution was added dropwise to the DLDPE solution or H_2SO_4 solution with constant stirring, and after the pH of the mixed solution stabilized, the volume of solution added dropwise and the pH were recorded, and a curve of pH versus the volume added dropwise was plotted.

Crosslinker: DLDPE was dissolved in NaOH solution followed by thiourea dioxide, and the reaction was stirred at 70 ^{o}C for 6 h. At the end of the reaction, the pH of the reaction solution was adjusted to 1 with H_2SO_4, and a large amount of solids was precipitated. The solids were collected by filtration, and the solids were dried in a vacuum oven at 80 ^{o}C to obtain the nitro reduction product rDLDPE. The rDLDPE was added to diethylenetriamine and the reaction was stirred at 140 ^{o}C for 5 h. After the reaction was cooled to room temperature, excess water was added, the product was extracted with n-butanol, and the solvent was removed by evaporation to obtain a transparent brown-red paste rDLDPE-NH_2. rDLDPE-NH_2 was dissolved in THF, and a THF solution of terephthalaldehyde was prepared in the ratio of aldehyde group: amino group of 1:1. The two solutions were mixed to obtain the prepolymerization solution, which was heated at 70 oC for 1 h and then transferred to a circular PTFE mould. The prepolymerisation solution was evaporated at room temperature for 12 h and then in an oven at 80 ^{o}C for 12 h. Finally, the reddish-brown transparent film CAN-rDLDPE/TPA was obtained.

CAN-rDLDLPE/TPA fragments were added to 1 M HCl/THF solution and stirred at room temperature for 30 min. after the reaction, excess water was added to the reaction solution and a large white precipitate precipitated. The white precipitate TPA was collected by filtration and the pH of the filtrate was adjusted with 1M NaOH solution to 11. The filtrate was extracted with n-butanol to obtain rDLDLPE-NH_2.

Degradation of real-life polyolefins

The collected PP colour box, PP syringe, LDPE disposable glove and HDPE wash bottle were each cut into 0.5 cm×0.5 cm flakes. 0.4 g single polyolefin flakes and 5 mL 4 M HNO_3 were added to a 50 mL hydrothermal synthesis kettle and placed in a PTFE magnetic stirrer. The kettle was sealed and heated in an oil bath at 140 ^oC for 2 h. After cooling the kettle to room temperature with cold water, the kettle was opened and the solids were collected by filtration, and the solids were dissolved with DCM. The pigments in the PP colour boxes were insoluble in DCM after degradation; the degraded solids of the LDPE disposable gloves and the HDPE wash bottles were completely dissolved in DCM.

PP syringe, LDPE disposable glove and HDPE bottles were cut into 0.5 cm×0.5 cm flakes. 0.2 g each of the three plastic flakes and 5 mL 4 M HNO_3 were added in a 50 mL hydrothermal synthesis kettle with a PTFE magnetic stirrer. The kettle was sealed and heated in an oil bath at 140 ^oC for 2 h. After cooling the kettle to room temperature with cold water, the kettle was opened, the solids were collected by filtration, and the solids were dissolved with DCM.

Mineral water bottle was disassembled into LDPE film, HDPE cap, and PET bottle and cut into 0.5 cm×0.5 cm flakes. 0.2 g each of the three plastic flakes and 5 mL 4 M HNO_3 were added in a 50 mL hydrothermal synthesis kettle with a PTFE magnetic stirrer. The kettle was sealed and heated in an oil bath at 140 ^oC for 2 h. After cooling the kettle to room temperature with cold water, the kettle was opened and the solids were collected by filtration. The solids were dissolved with DCM.

Analysis instruments

Fourier-Transform Infrared Spectroscopy (FT-IR). FT-IR spectroscopy was performed on a Nicolet 6700 FT-IR System. Infrared testing was performed using potassium bromide compressions with a wave number range of 4000-400 cm^{-1}.

Nuclear Magnetic Resonance (NMR). The degradation products were analyzed by a Bruker Avance 400 Fouriertransform nuclear magnetic resonance spectrometer operating at 400 MHz. $CDCl_3$ was tested as a deuterated reagent.

Gel permeation chromatography (GPC). Molecular weight distributions were analyzed on an Agilent PL-GPC 220 gel permeation chromatograph, equipped with a PL-Gel Mixed B guard column, three PL-Gel Mixed B columns, and a refractive index (RI) detector. THF was used as a mobile phase. Molecular weight was determined from a calibration curve obtained using polystyrene standards.

High temperature gel chromatography were analyzed on an Agilent PL-GPC 220 gel permeation chromatograph, equipped with PL-Gel MIXED-B LS column, and a refractive index (RI) detector. 1,2,4-TCB (stabilized with BHT) was used as a mobile phase at 150 ^{o}C. Molecular weight was determined from a calibration curve obtained using polystyrene standards.

Organic Elemental Analysis (EA). The samples were incubated in a vacuum oven at 80 ^{o}C for 12 h. All experiments were carried out on Germany elementar vario EL cube in CHN analysis mode and each sample was tested twice in parallel.

Tensile property test. The experiments were carried out in an electronic universal material testing machine, INSTRON 3366, Instron, USA. The load cell was 1 kN and the clamp tension rate was 1 mm/min. At least 5 valid data were obtained for each set of specimens and the mean and standard deviation were calculated.

Figures

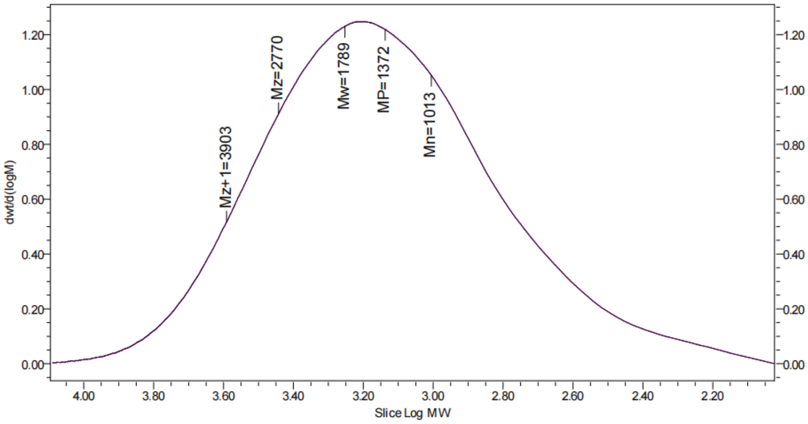

Figure S1. GPC curve of DLDPE.

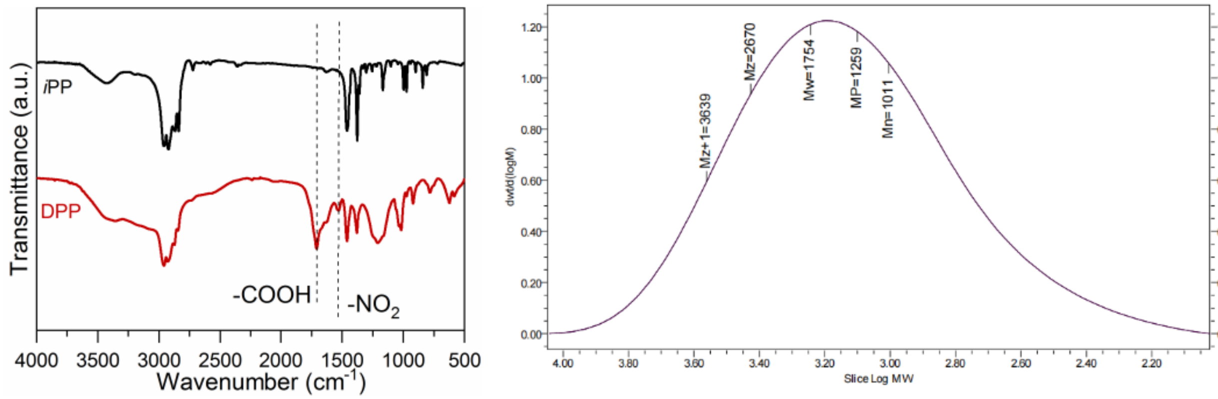

Figure S2. IR spectra and GPC curves of DPP

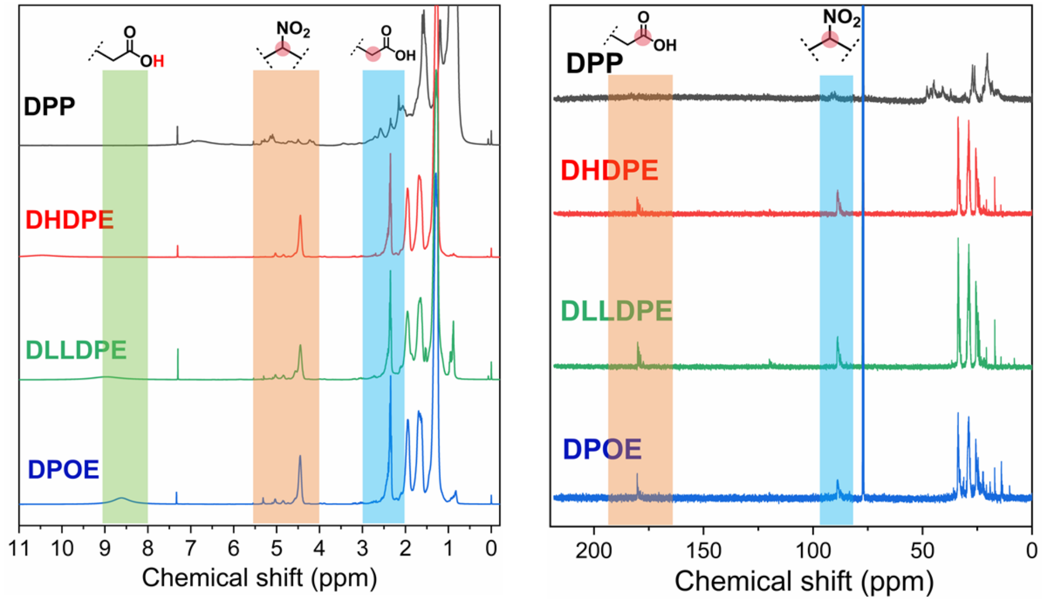

Figure S3. ^{1}H and ^{13}C NMR spectra of different polyolefin degradation products in $CDCl_3$

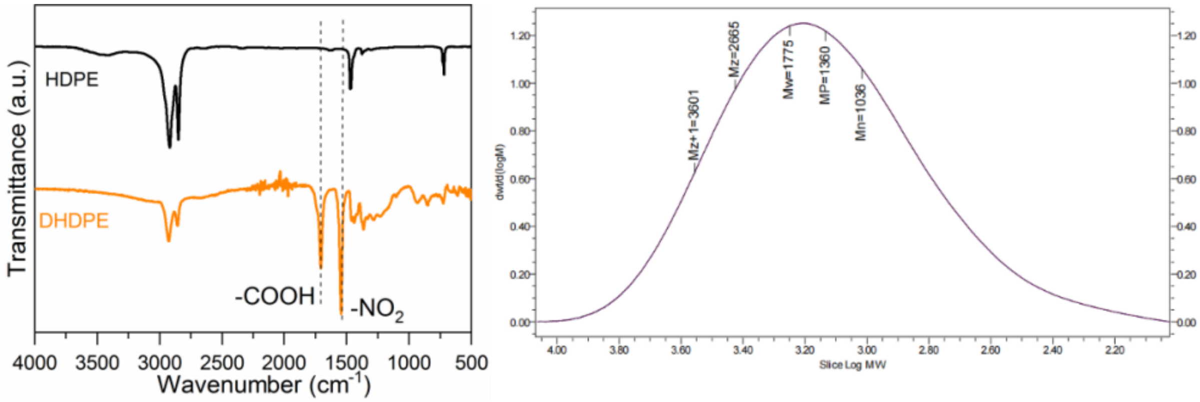

Figure S4. IR spectra and GPC curves of DHDPE.

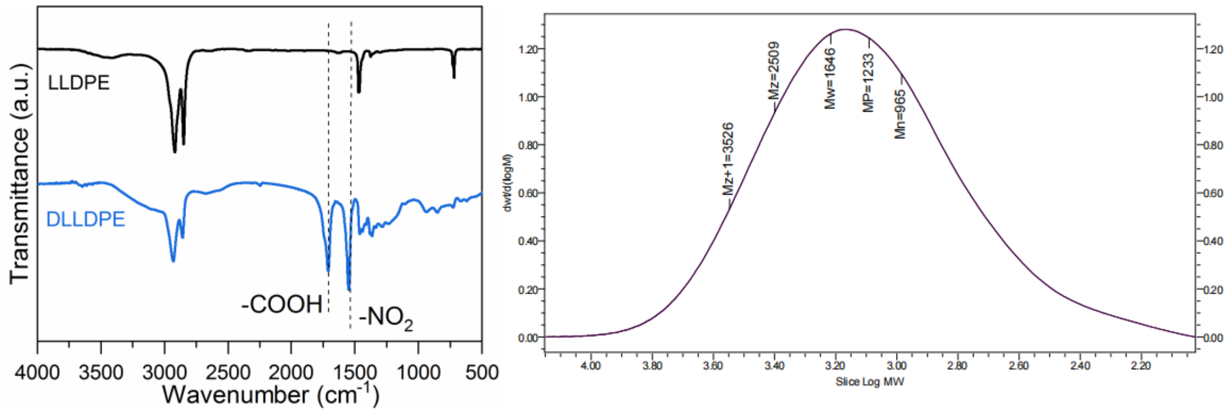

Figure S5. IR spectra and GPC curves of DLLDPE.

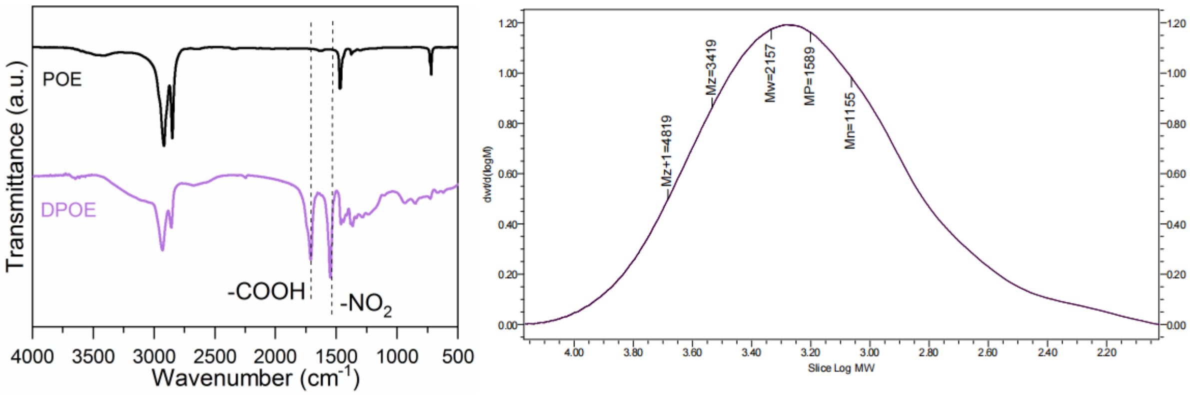

Figure S6. IR spectra and GPC curves of DPOE.

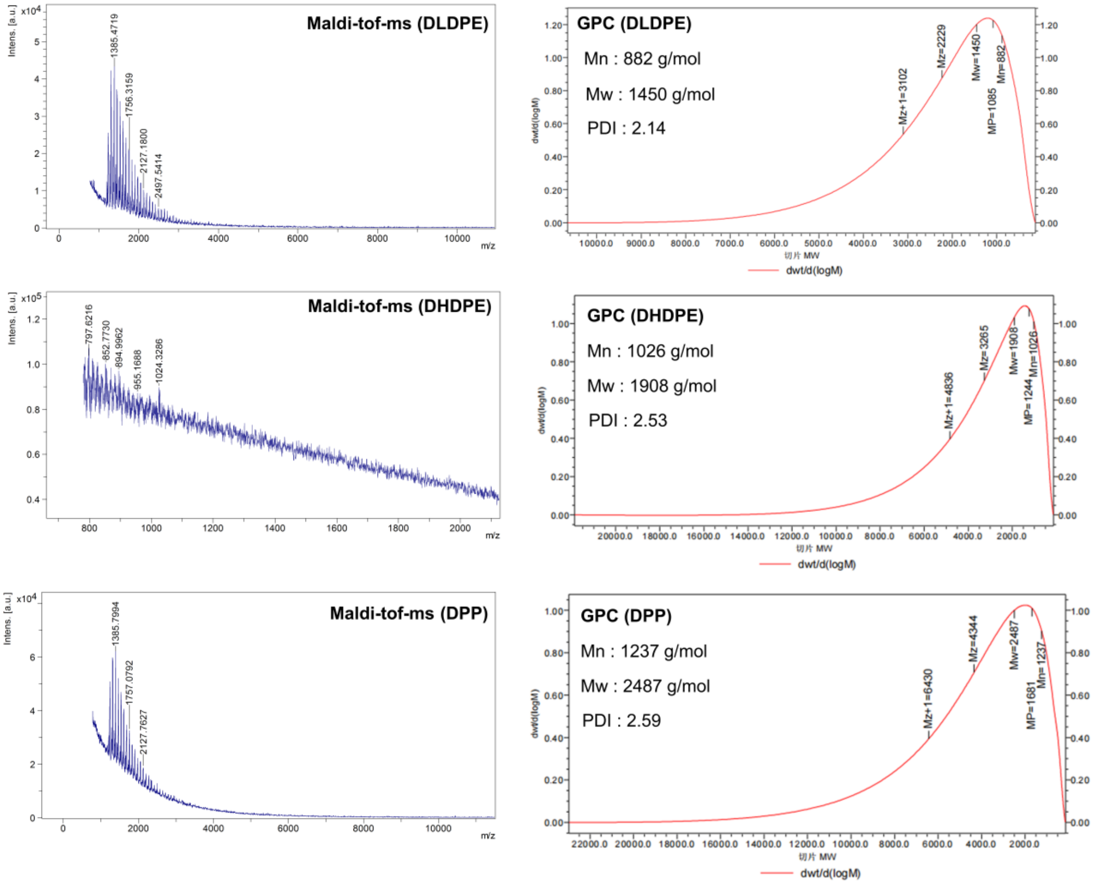

Figure S7. MALDI-TOF-MS and GPC analysis of three polyolefin degradation products

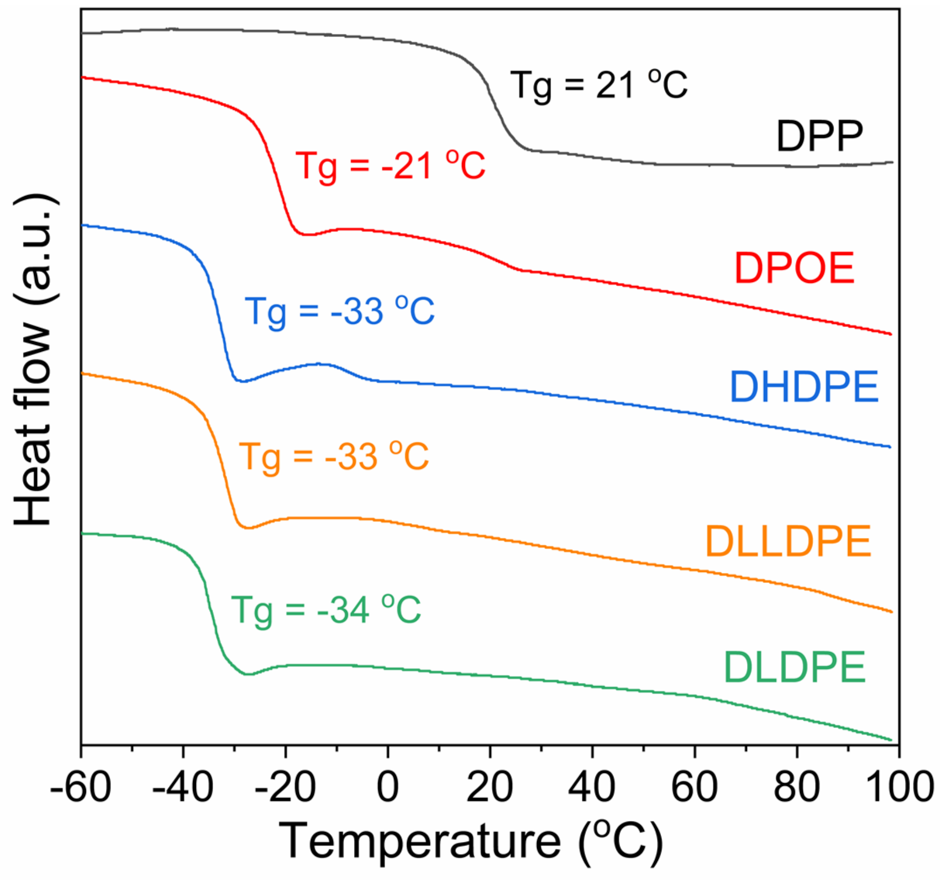

Figure S8. DSC curves of five polyolefin degradation products

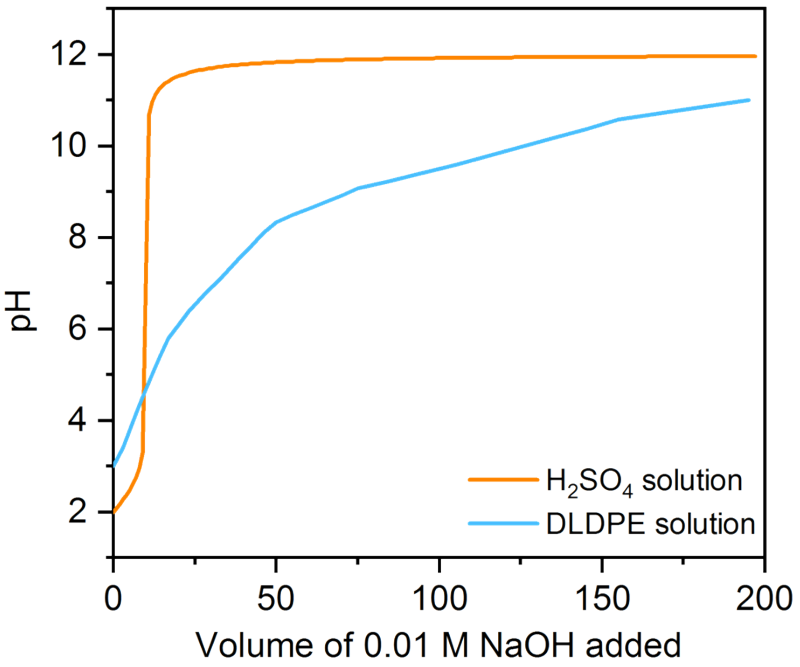

Figure S9. Variation curve of solution pH with NaOH addition.

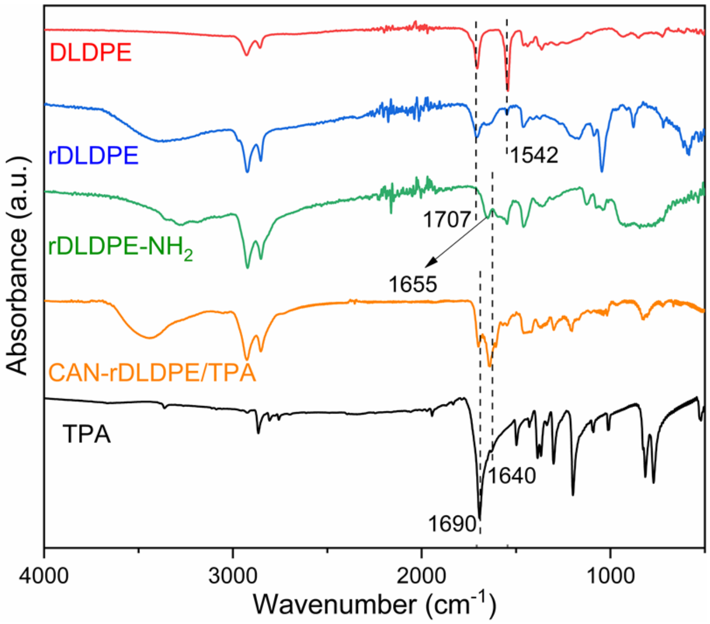

Figure S10. IR spectra of DLDPE, rDLDPE, rDLDPE-NH2, TPA, and CAN-rDLDPE/TPA.

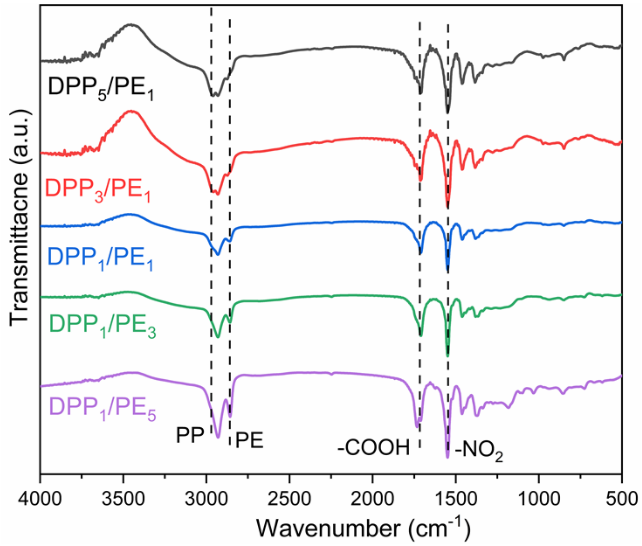

Figure S11. IR spectra of degradation products from different ratios of PP:PE

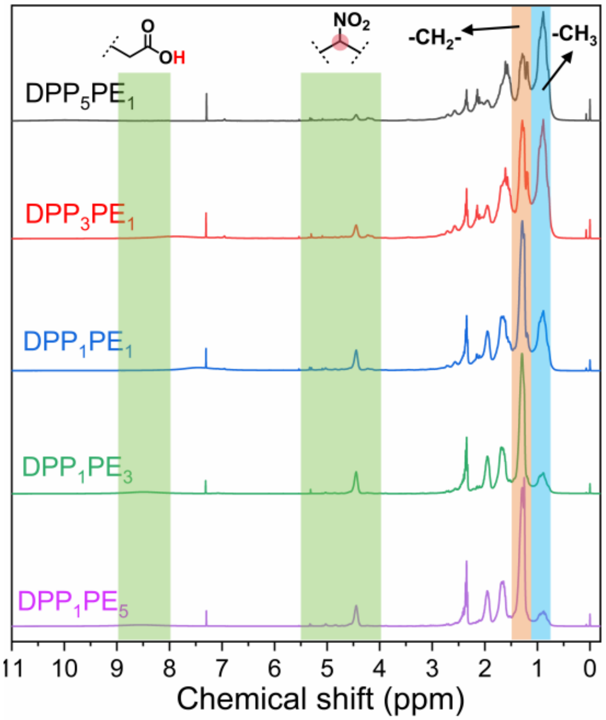

Figure S12. ^{1}H NMR spectra of mixed degradation products under different PP/PE in $CDCl_3$

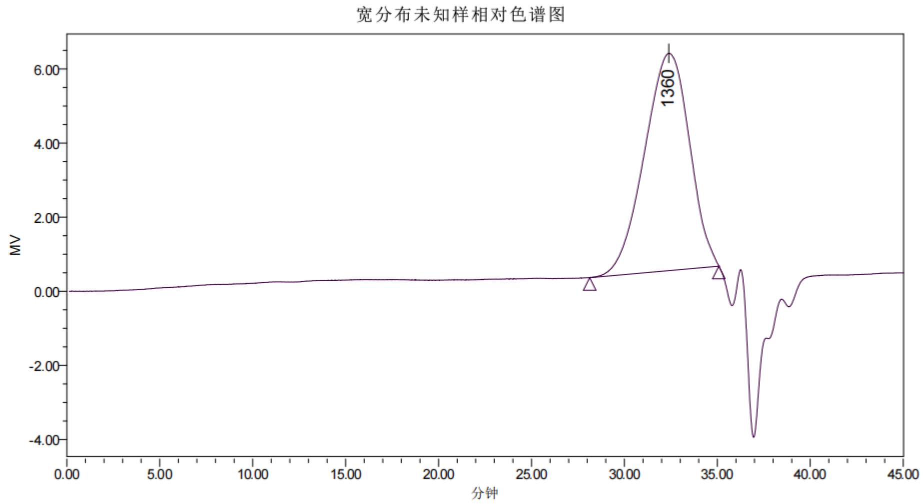

Figure S13. GPC chromatogram of mixed degradation product DPP_5/PE_1

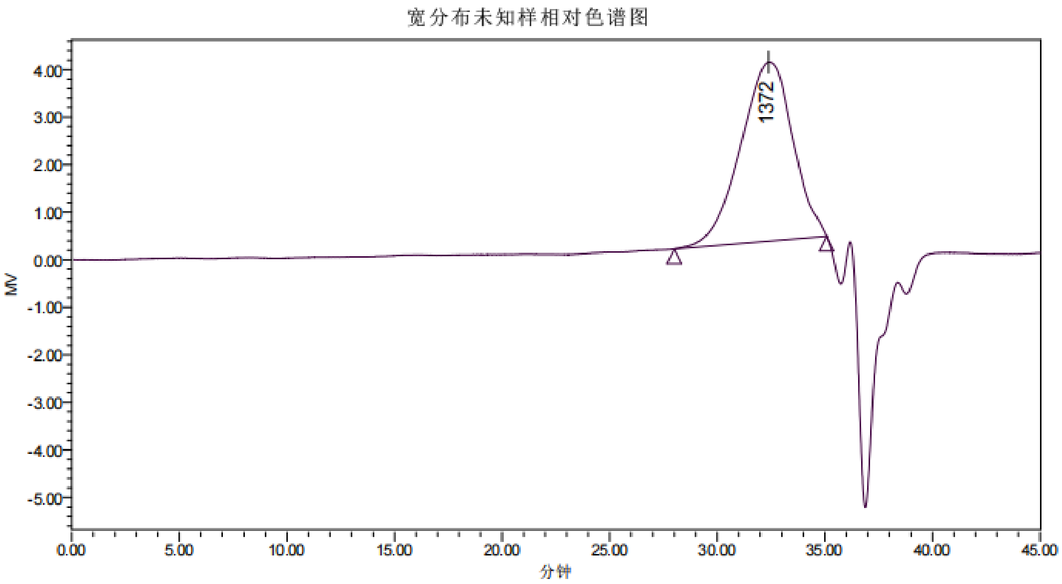

Figure S14. GPC chromatogram of mixed degradation product DPP_3/PE_1

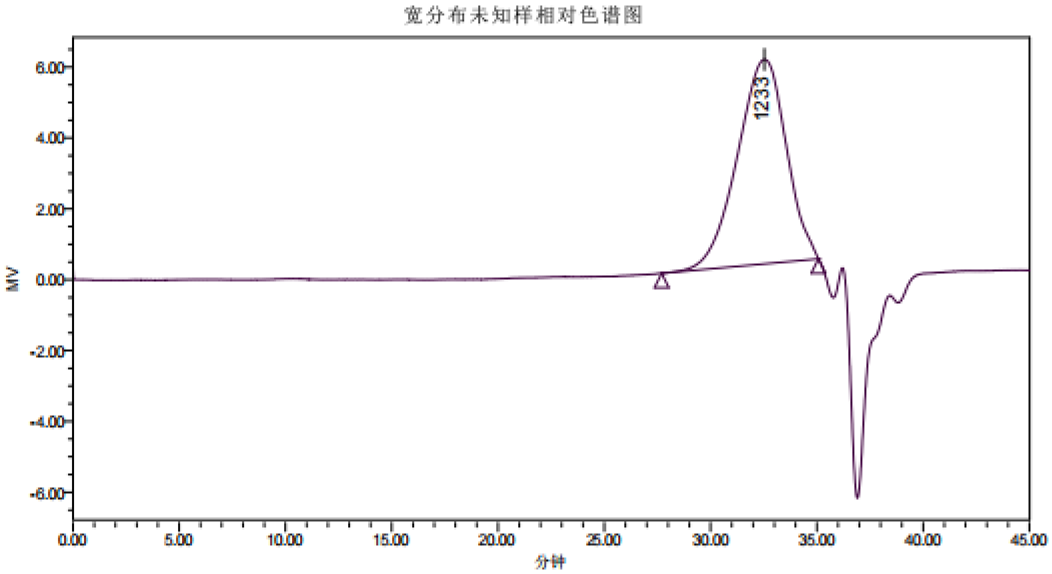

Figure S15. GPC chromatogram of mixed degradation product DPP_1/PE_1

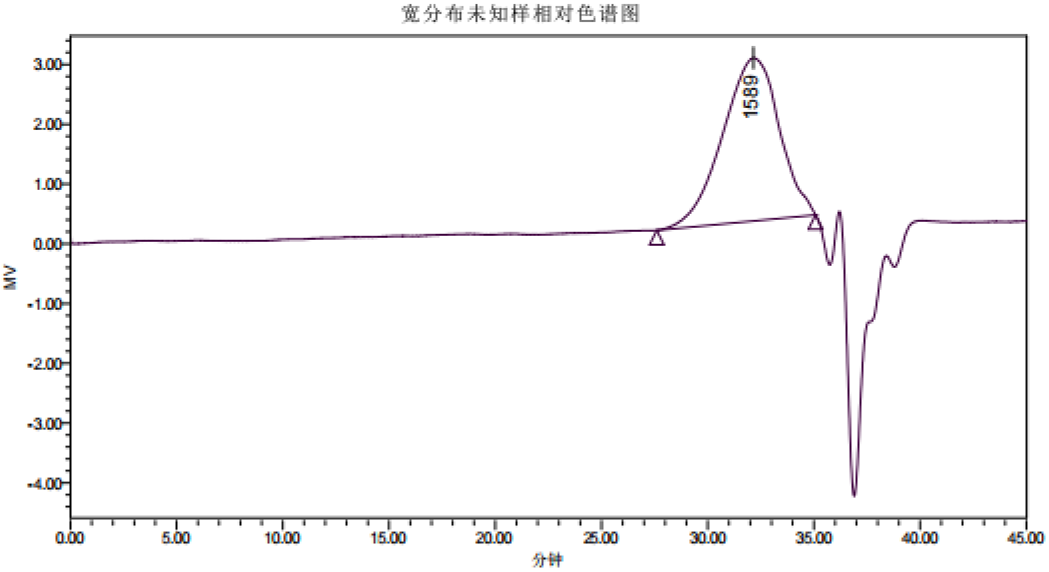

Figure S16. GPC chromatogram of mixed degradation product DPP_1/PE_3

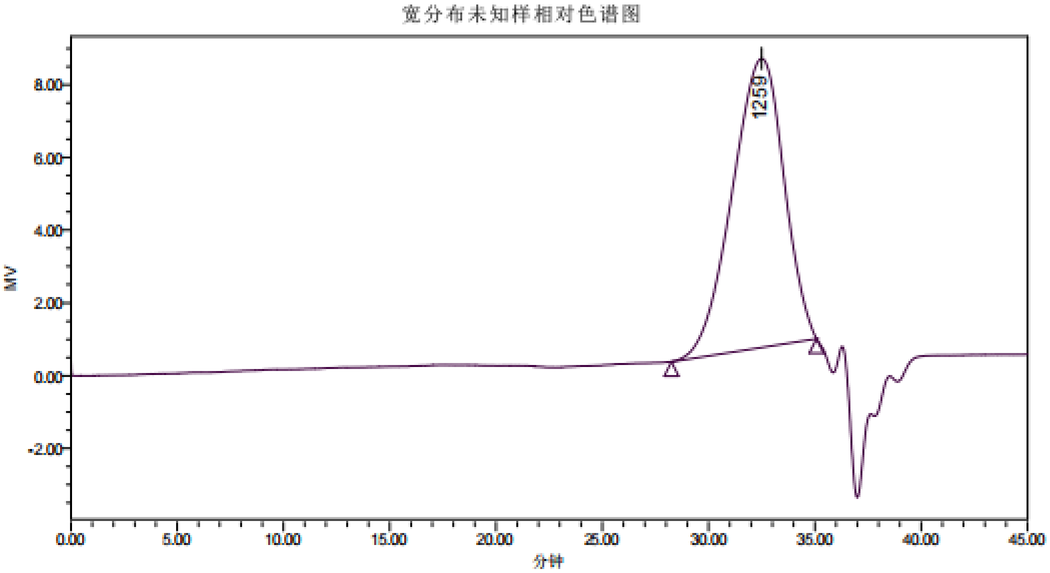

Figure S17. GPC chromatogram of mixed degradation product DPP_1/PE_5

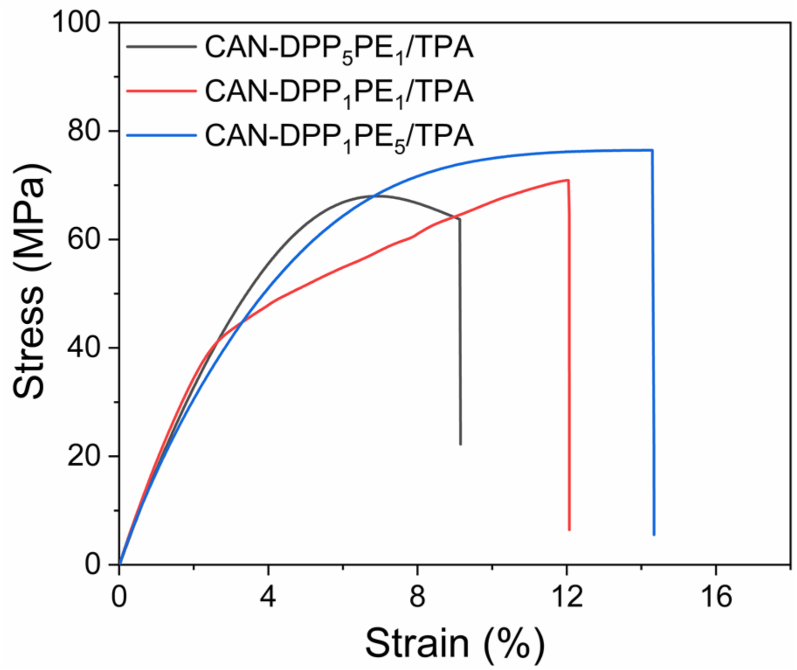

Figure S18. Stress-strain curves of imines synthesized from mixed degradation products under different PP/PE

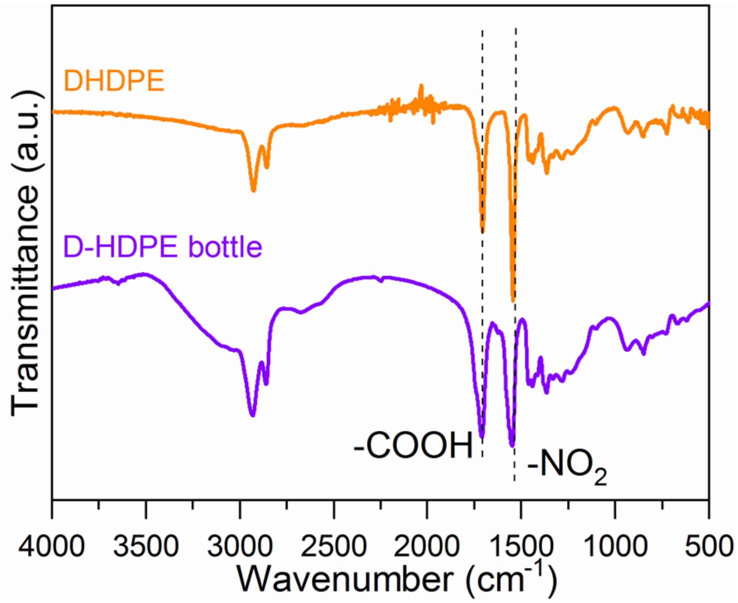

Figure S19. IR spectra of degradation product from HDPE bottle.

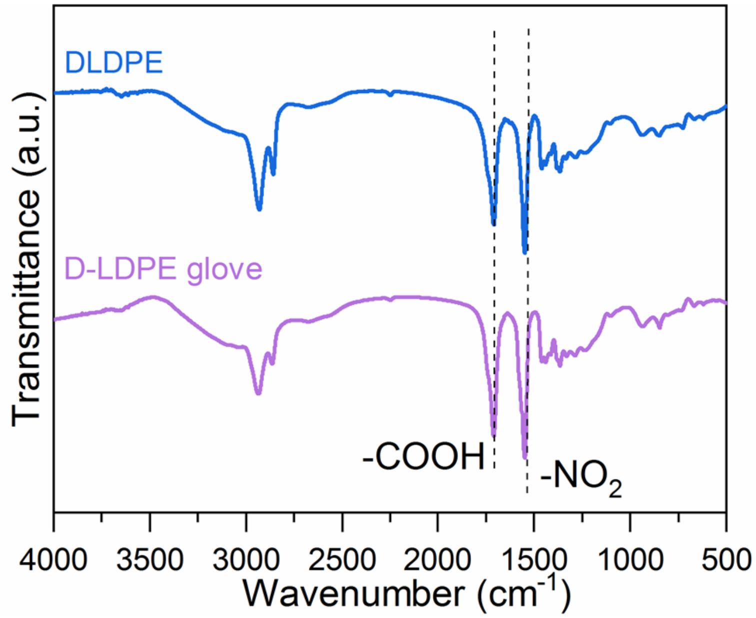

Figure S20. IR spectra of degradation product from LDPE glove.

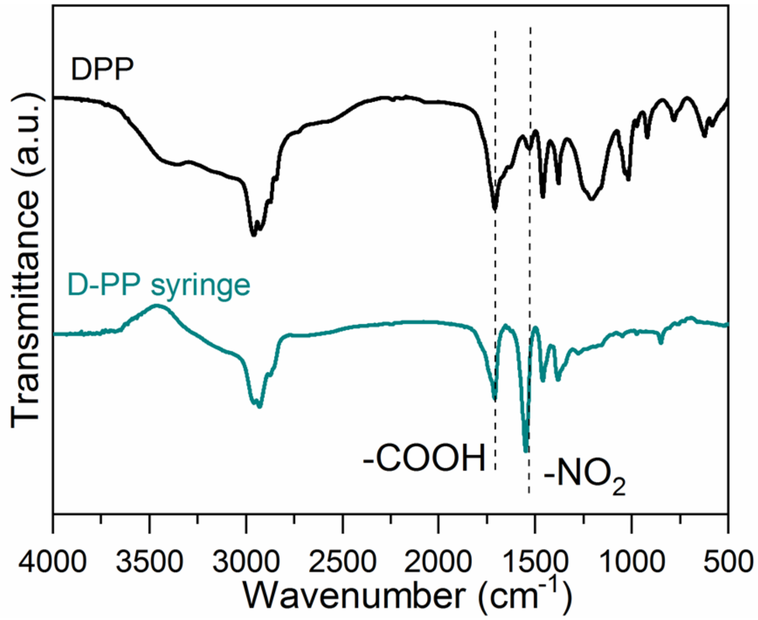

Figure S21. IR spectra of degradation product from PP syringe glove.

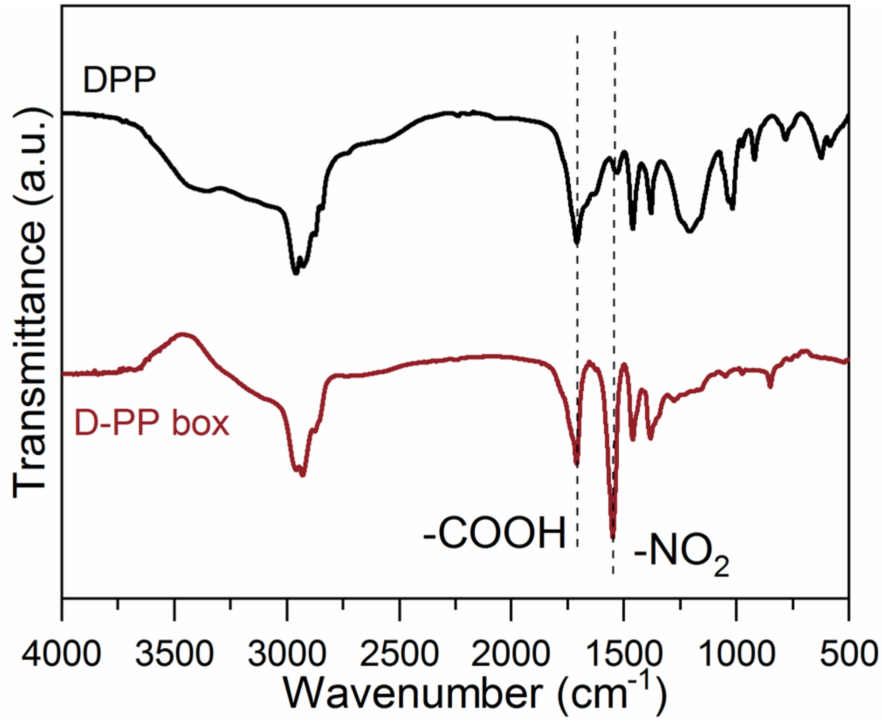

Figure S22. IR spectra of degradation product from PP box.

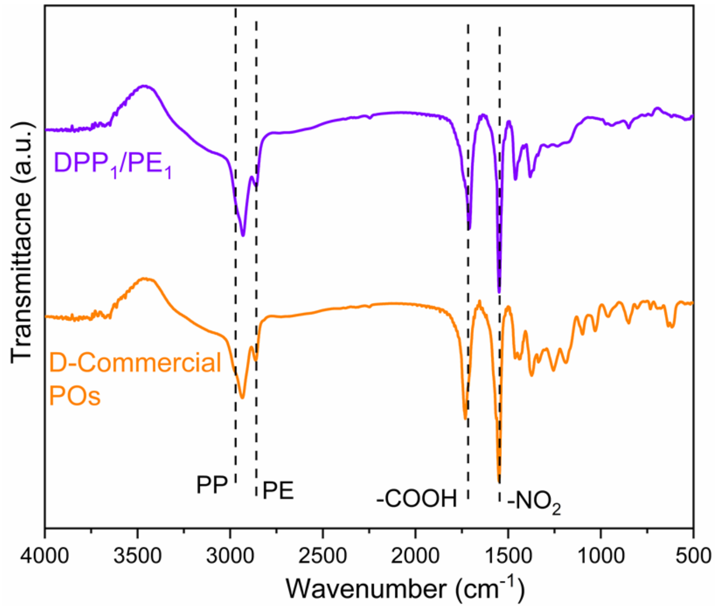

Figure S23. IR spectra of degradation products from mixed PP syringe, HDPE bottle and LDPE glove.

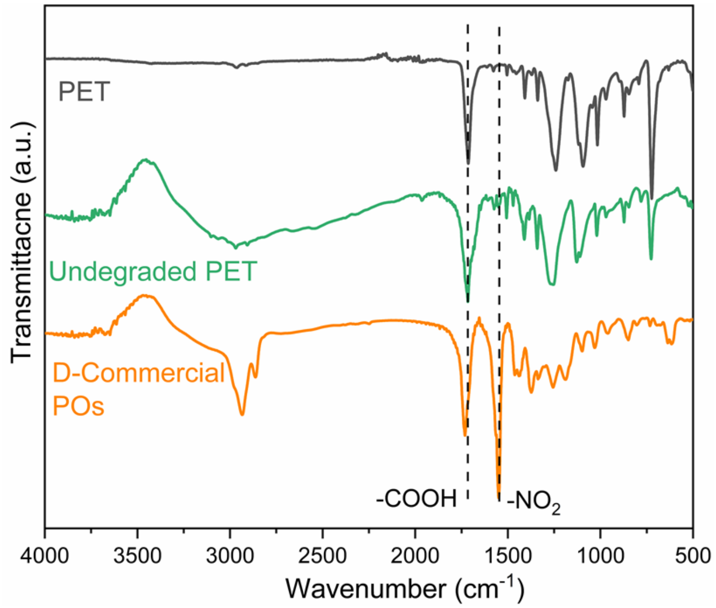

Figure S24. IR spectra of degradation products from mixed LDPE film, HDPE cap and PET bottle.

Tables

T °C	t h	HNO_3 mol/L	DLDPE Yield wt%	 NO_2 mmol/g	 COOH mmol/g	 Mn g/mol	 PDI
140	1	4	108.1	1.7	0.6	9647	3.1
140	1.5	4	123.9	6.0	2.6	1325	2.5
140	2	4	118.2	5.7	2.6	1115	2.2
140	2.5	4	110.6	5.7	2.7	1096	2.3
140	3	4	109.4	6.2	3.2	1076	2.0
140	4	4	105.3	6.7	3.3	1075	1.8
140	3	2	99.7	0.7	0.4	9912	2.9
140	3	6	77.2	5.9	4.1	734	1.9
120	3	4	111.8	2.6	0.9	6262	2.7
160	3	4	90.1	5.1	3.0	726	1.7

Table S1. Degradation products of LDPE under different conditions.

T °C	t h	HNO_3 mol/L	DPP Yield wt%	 NO_2 mmol/g	 COOH mmol/g	 Mn g/mol	 PDI
140	1	4	97.5	1.3	1.0	6684	3.1
140	1.5	4	115.3	4.1	2.0	1132	2.5
140	2	4	106.4	3.9	2.1	1124	2.2
140	2.5	4	101.4	3.5	2.1	1067	1.8
140	3	4	97.5	3.4	2.2	996	1.4
140	4	4	98.4	3.4	2.2	980	1.6

Table S2. Degradation products of PP at different reaction times.

PP:PE	DPP_x/PE_y				
	Yield wt%	NO_2 mmol/g	COOH mmol/g	Mn g/mol	PDI
5:1	107.6	4.0	2.5	1241	1.5
3:1	110.5	4.5	2.7	1185	1.8
1:1	112.4	5.2	3.1	1211	2.1
1:3	118.8	5.6	3.5	1086	1.9
1:5	122.3	6.2	3.9	1121	1.7

Table S3. Degradation products of mixed PP/PE in 4 M HNO_3 at 140 ^{o}C for 2 h.

Real-life plastics	DPO				
	Yield wt%	NO_2 mmol/g	COOH mmol/g	Mn g/mol	PDI
PP box	104.2	3.8	2.2	1054	1.8
PP syringe	108.4	4.1	2.1	997	1.4
HDPE bottle	116.3	5.4	3.0	995	1.6
LDPE glove	121.5	6.2	3.7	1132	2.1
PP syringe ,HDPE bottle and LDPE glove	114.2	5.1	3.1	1087	2.2
HDPE cap, PET bottle, and LDPE film	118.5	5.8	3.3	1157	1.9

Table S4. Degradation products of real-life plastics in 4 M HNO_3 at 140 ^oC for 2 h.