Supplementary Information

Tandem oxidative and thermal cracking of polypropylene at low temperature

Xiangyue Wei[1], Qiang Zhang[1], Chengfeng Shen[1], Xu Zhao[1], Fan Zhang[1], Xuehui Liu[2], Gang Wu[1], Shimei Xu[1]*, Yu-Zhong Wang[1]*

[1]The Collaborative Innovation Center for Eco-Friendly and Fire-Safety Polymeric Materials (MoE), National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), College of Chemistry, Sichuan University; Chengdu 610064, China.

[2]The Collaborative Innovation Center for Eco-Friendly and Fire-Safety Polymeric Materials (MoE), National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), College of Architecture and Environment, Sichuan University; Chengdu 610064, China.

*Corresponding author. Email: xushimei@scu.edu.cn; yzwang@scu.edu.cn

Materials

Polypropylene pellets (PP-T30S, Mw=4.20×105 g/mol, PDI 3.52) were purchased from China National Petroleum Corporation. $FeSO_4 \cdot 7H_2O$ were purchased from Jinshan Chemical Test. Sodium dodecyl sulfate (SDS, ≥99.0%) were purchased from Adamas-Beta. Cetyltrimethylammonium Bromide (CTAB, ≥99.0%) and 30% H_2O_2 (AR) were purchased from Chron Chemicals. Xylene (AR) and THF (AR) were purchased from Tianjin Zhiyuan Reagent Co. Ltd.

Methods

Oxidative Degradation of PP

PP (3 g) was added to 10 mL of dodecane and heated at 160^oC for 10 min under stirring. Afterwards, the PP was precipitated from the solution with temperature cooling. Solvent dodecane was recovered by filtration and recycled. The treated PP was soaked with ethanol for 12 h to wash away little dodecane from the molecular chain, and then dried at 80^oC followed by crushing into powder (80 to 100 mesh) for degradation experiment.

Degradation experiments were performed in a hydrothermal synthesis kettle with a 40 mL PTFE liner. Typically, 0.16 g SDS and 0.40 g PP powder (SDS: PP=0.4:1(w/w)) were added to 3.6 mL of 30% H_2O_2 under magnetically stirring. $FeSO_4 \cdot 7H_2O$ (7 mg) was added after PP was fully wetted and dispersed well. The hydrothermal synthesis kettle was quickly sealed and transferred to an oil bath at 80^oC for 30 min with a stirring speed of 600 rpm. After the reaction was completed, the hydrothermal synthesis kettle was placed in cold water to quench the reaction. After cooling down to room temperature, the reaction gases were collected using a gas bag while the solids and liquids were separated by filtration.

The solid products are dissolved in THF and the insoluble fraction was filtrated off. The solvent was evaporated by a rotary evaporator to obtain a yellow paste (the main solid product DPP-THF). The fraction insoluble in THF was transferred to xylene and the mixture was heated at 100°C for 30 min followed by immediate filtration. The insoluble residue was a small amount of black powder (Char), while the solution fraction was evaporated to obtain a light-yellow powder (DPP-Xylene). Solvents used in the dissolution and separation process, such as THF and xylene, can be collected by evaporation and recycled.

After degradation, the solution was highly acidic (pH 1). To characterize and quantify the acid, a methyl ester derivatization reaction was carried out using 4 mL of the degradation solution and 15 mL of 20% H_2SO_4-CH_3OH at 60°C for 6 h. The derivatized degradation solution was extracted with dichloromethane for GC-FID and GC-MS analysis. The succinic acid in the degradation solution was quantified by the standard curve of dimethyl succinate. The total amount of organic matter in the degradation solution was determined by TOC analysis. In addition to the degradation products of PP, the decomposition products of SDS are also mainly included in the degradation solution. A certain amount of the degradation solution was extracted with DCM to remove most of the organic components. The concentration of SO_4^{2-} in the extracted degradation solution was measured by anion chromatography. After deducting SO_4^{2-} in the raw material, the decomposition rate of SDS was calculated according to the remaining SO_4^{2-} concentration. Next, the amount of undecomposed SDS in the degradation solution was measured by methylene blue spectrophotometry.

The reaction gases composition was determined by GC-TCD analysis. The gaseous products are mainly CO_2 and a small amount of CO.

Adsorption of PP for Fe^{2+} in the reaction solution

The adsorption capacity of PP for Fe^{2+} in SDS or CTAB solution was studied. 0.16 g of SDS or CTAB were added to 5 mL H_2O, then 0.4 g of PP powder, and 7 mg of $FeSO_4 \cdot 7H_2O$ were added. The mixture was allowed to stand for 10 min at room temperature until the adsorption equilibrium. The Fe^{2+} concentration in the supernatant was measured by phenanthroline spectrophotometry, and the adsorption amount of PP to Fe^{2+} was calculated.

Monitoring of reaction internal temperature

The degradation reactions were carried out in a reactor with the temperature sleeve. The internal temperature of the reaction was tested three times in parallel and the sensor sensitivity of the measured temperature was at ± 0.5°C. In order to prevent the metal sleeve from affecting the degradation reaction, the temperature measuring point was designed above the reaction liquid level. The temperature of the gas in the reactor was measured, and the test temperature would be lower than the actual reaction temperature. The internal temperature of the reaction for different ratios of SDS to PP was recorded, and the curve of the internal temperature with time was plotted.

Degradation of commercial PP

Three commercial PPs (PP food packing box, PP centrifugal tube, and PP colored packing box) were pulverized into powder in the same way as PP-T30S. The degradation of commercial PP was carried out according to the optimal conditions for PP-T30S degradation. 0.4 g commercial PP powder and 0.16 g SDS (SDS:PP=0.4:1(w/w)) were added to 3.6 mL of 30% H_2O_2 under magnetically stirring. $FeSO_4 \cdot 7H_2O$ (7 mg) was added after PP was wetted and stirred well. The hydrothermal synthesis kettle was quickly sealed and transferred to an oil bath at 80^{o}C for 30 min with stirring speed of 600 rpm. After the reaction was completed, the hydrothermal synthesis kettle was placed in cold water to quench the reaction. The products are separated in the same way as before.

Analysis and calculation

Yield and carbon balance

The yields of three solid products including DPP-THF ($Yield_{DPP\text{-}THF}$), DPP-Xylene ($Yield_{DPP\text{-}Xylene}$) and Char ($Yield_{Char}$) were calculated using eq. S1 respectively.

$$Yield_{solid\ product}(wt\%) = \frac{mass\ of\ solid\ product}{mass\ of\ initial\ PP} \times 100\% \qquad \text{S1}$$

The yield of major liquid product succinic acid was calculated using eq. S2

$$Yield_{succinic\ acid}(wt\%) = \frac{mass\ of\ succinic\ acid}{mass\ of\ \ PP + mass\ of\ SDS} \times 100\% \qquad \text{S2}$$

Reaction carbon balance. The carbon in the reaction feedstock SPP and SDS was transferred to the gaseous, solid and liquid products, where the percentage of carbon in the gaseous products was calculated by eq. S3.

$$C_{gas}(\%) = 1 - C_{solid} - C_{liquid} \qquad \text{S3}$$

C_{solid} in the equation was obtained by organic elemental analysis of the solid product, and C_{liquid} was obtained by TOC analysis of the degradation solution.

Solid product characterization analysis

Content of methyl ketone and isopropenyl groups. ^{1}H NMR was performed on a mixture of DPP-THF and 2.0 μL DCE in $CDCl_3$. The contents of methyl ketone and isopropenyl groups are calculated using eq. S5-S7.

$$mol\ of\ i\text{sopropenyl}\ (mmol) = \frac{\text{integration}\ of\ i\text{sopropenyl}}{\text{integration}\ of\ DCE} \times mol\ of\ DCE \times \frac{4}{2} \qquad \text{S4}$$

$$mol\ of\ methyl\ ketone\ (mmol) = \frac{\text{integration } of\ Methy\ ketone}{\text{integration } of\ DCE} \times mol\ of\ DCE \times \frac{4}{3} \qquad \text{S5}$$

$$Content\ of\ functional\ group\ (mmol/g) = \frac{mol\ of\ function\ group}{mass\ of\ DPP{-}THF} \qquad \text{S6}$$

Content of carboxyl group. A 10 g/L phenolphthalein ethanol solution and a 0.02 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: 20 mg of DPP-THF ($W_{\text{DPP-THF}}$) 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 $V_{\text{DPP-THF}}$, and the carboxylic acid content in DPP-THF was calculated after deducting the blank volume V_{blank}(eq. S7).

$$\text{Carboxyl content } (mmol/g) = \frac{(V_{DPP-THF} - V_{blank}) \times 10^{-3} \times C_{KOH} \times 10^{3}}{W_{DPP-THF} \times 10^{-3}} \qquad \text{S7}$$

Thermodynamic analysis

The thermodynamic data of oxidative cracking and thermal cracking of PP were calculated by Benson Group contribution method. The molar formation enthalpy and molar entropy of the substance were calculated as follows.

$$\Delta_f H_m^{\theta}(A) = \Sigma_k N_k \Delta_f H_{m,k}^{\theta} \qquad \text{S8}$$

$$S_m^{\theta}(A) = \Sigma_k N_k S_{m,k}^{\theta} + S_{m,s}^{\theta} \qquad \text{S9}$$

A represents the substance involved in the reaction, k represents the groups, and $S_{m,s}^{\theta}$ is the symmetric entropy of substance A.

The thermodynamic equations for the chemical reaction are as follows.

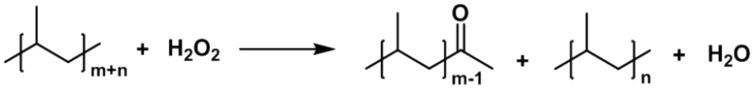
$$\Delta_r H_m^\theta = \Sigma_A \upsilon_A \Delta_f H_m^\theta(A) \tag{S10}$$

$$\Delta_r S_m^\theta = \Sigma_A \upsilon_A S_m^\theta(A) \tag{S11}$$

$$\Delta_r G_m^\theta = \Delta_r H_m^\theta - T\Delta_r S_m^\theta \tag{S12}$$

υ_A is the stoichiometric number of the reaction.

The contribution values of the groups are in Extended Data Table 3. The chemical equation for the oxidation cracking of PP to form methyl ketone is:

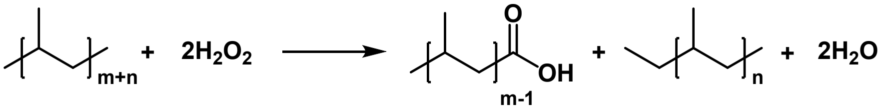


The total contribution of groups to this reaction is:

$$G_{r,m}(oxidation\ craking) = -2G_2 - G_3 + G_4 + G_5 + G_6 + G_{13} - G_{14} \tag{S13}$$

From this, the thermodynamic data for the oxidation cracking of PP were calculated ($\Delta_r H_{m,1}^\theta = -251.9\ kJ/mol$, $\Delta_r G_{m,1}^\theta = -296.2\ kJ/mol$).

The contribution values of the groups are in Extended Data Table 3. The chemical equation for the oxidation cracking of PP to form carboxyl is:

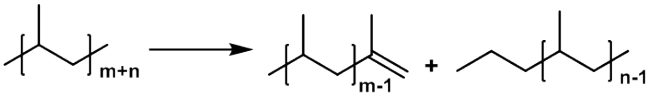


The total contribution of groups to this reaction is:

$$G_{r,m}(oxidation\ craking) = -G_2 - G_3 + G_5 + G_7 + G_8 + 2G_{13} - 2G_{14} \tag{S14}$$

From this, the thermodynamic data for the oxidation cracking of PP were calculated ($\Delta_r H_{m,2}^\theta = -594.8\ kJ/mol$, $\Delta_r G_{m,2}^\theta = -620.3\ kJ/mol$).

The chemical equation for the thermal cracking of PP to form isopropenyl is:



The total contribution of groups to this reaction is:

$$G_{r,m}(thermal\ craking) = -G_1 - G_2 - 2G_3 + G_9 + G_{10} + G_{11} + G_{12} \tag{S15}$$

From this, the thermodynamic data for the thermal cracking of PP were calculated ($\Delta_r H_{m,3}^{\theta} = 86.1\ kJ/mol$, $\Delta_r G_{m,3}^{\theta} = 36.9\ kJ/mol$).

Analysis instruments

Gas chromatography

Methyl ester derivatized degradation solution and dimethyl succinate standard were analyzed quantitatively on an Agilent 7890B gas chromatograph equipped with a flame ionization detector (FID). Organic components in degradation solution were analyzed qualitatively on a GCMS-QP2010 Plus gas Chromatograph/Mass Spectrometer. Gas products were analyzed qualitatively on a Shimadzu GC-8AIT gas chromatograph equipped with a thermal conductivity detector (TCD), using Ar as the internal standard.

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 (^1H NMR) or 600 MHz (^{13}C NMR). $CDCl_3$ was tested as a deuterated reagent.

Gel permeation chromatography (GPC)

Molecular weight distributions of DPP-THF 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. The molecular weight of PP-T30S, DPP-Xylene and commercial PP is obtained by high temperature GPC test, which 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℃. Molecular weight was determined from a calibration curve obtained using polystyrene standards.

Total Organic Carbon

The test of dissolved organic carbon in degradation solution was performed on Analytik Jena MULTI N/C 2100S instrument.

Thermogravimetric and Differential Scanning Synchronous Thermal Analyzer (TGA/DSC)

The synchronous thermal analysis experiment of PP was conducted on METTLER TOLEDO TGA/DSC 1/110LF. The instrument is equipped with alumina crucible and air/nitrogen atmosphere. Gas flow rate is 50 ml/min and heating rate is 10 ^{o}C/min.

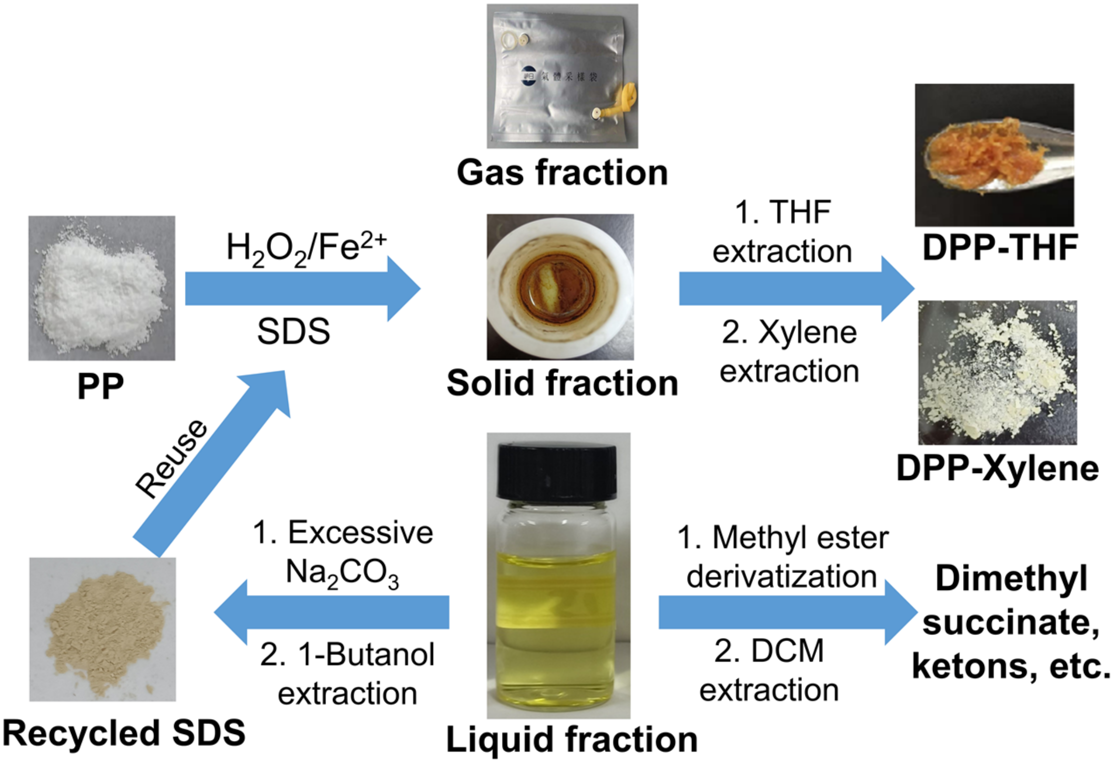


Fig. S1 Schematic separation path of degradation products.

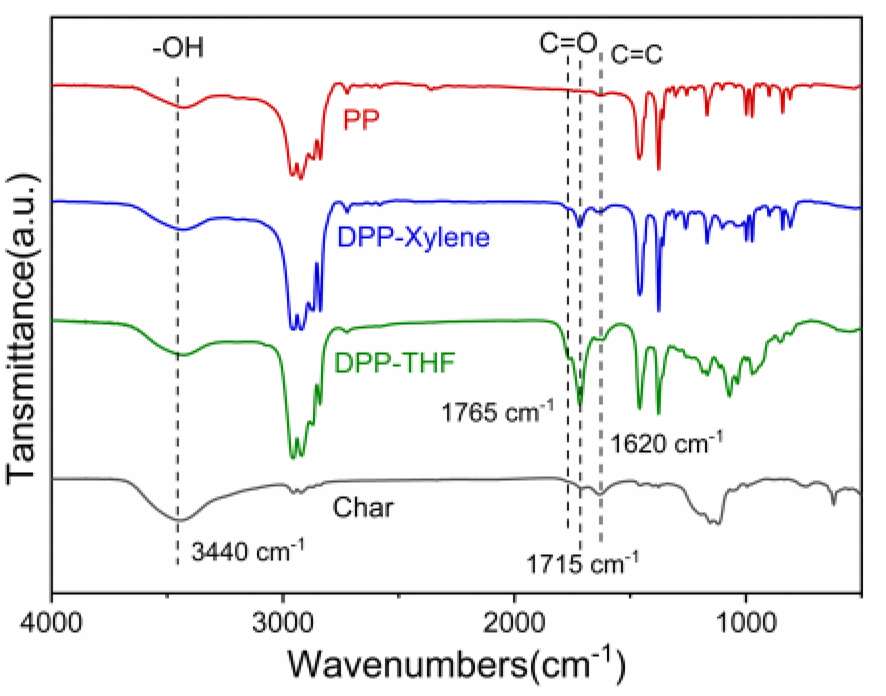


Fig. S2 FT-IR spectra of PP, DPP-Xylene, DPP-THF and Cha

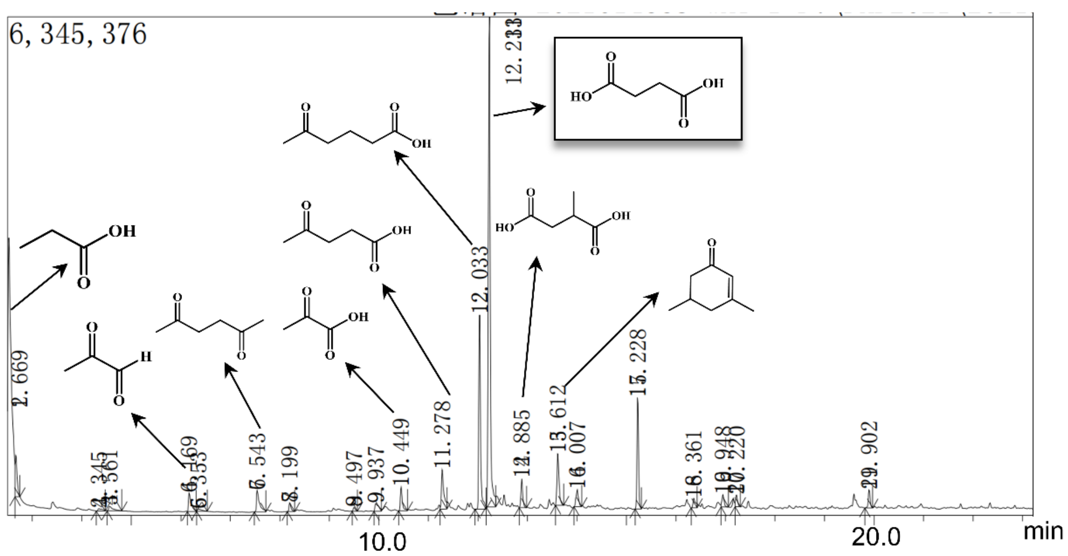


Fig. S3 GC-MS analysis of degradation solution by dichloromethane (DCM) extraction.

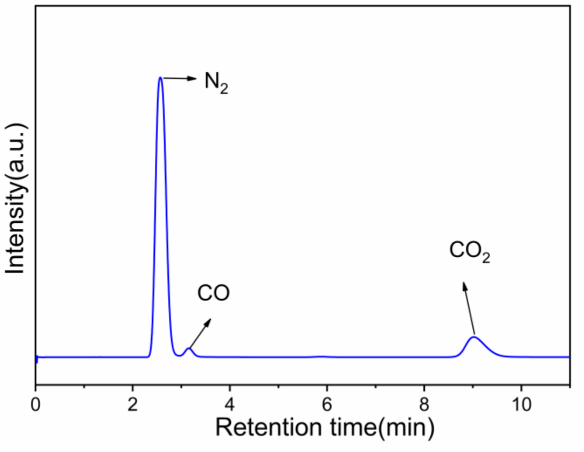


Fig. S4 GC-TCD of gases collected from the degradation of PP at 80°C for 30 min.

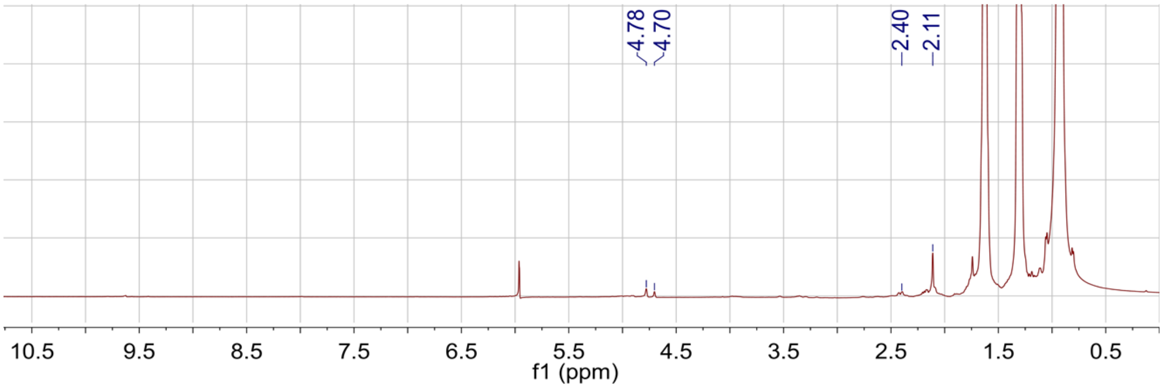


Fig. S5 400 MHz ^{1}H NMR spectra of DPP-Xylene in 1,1,2,2-$C_2D_2Cl_4$ at 120^{o}C.

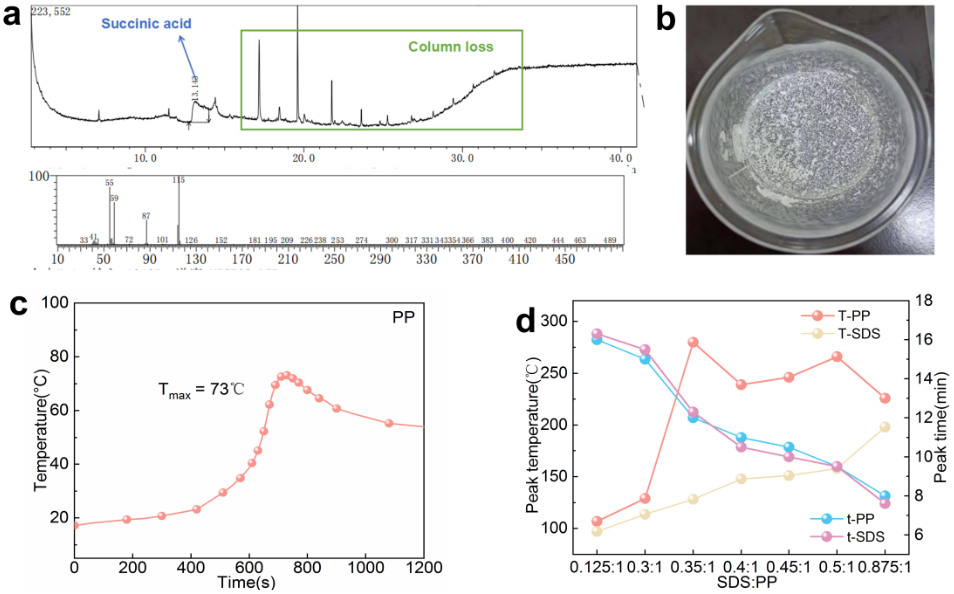


Fig. S6 (a) GC-MS analysis of SDS degradation solution. **(b)** Morphology of PP after degradation without SDS. **(c)** The oxidative degradation of PP without SDS. **(d)** The relationship of internal peak temperature and time in degradation reaction of PP varying the weight ratio of SDS to PP

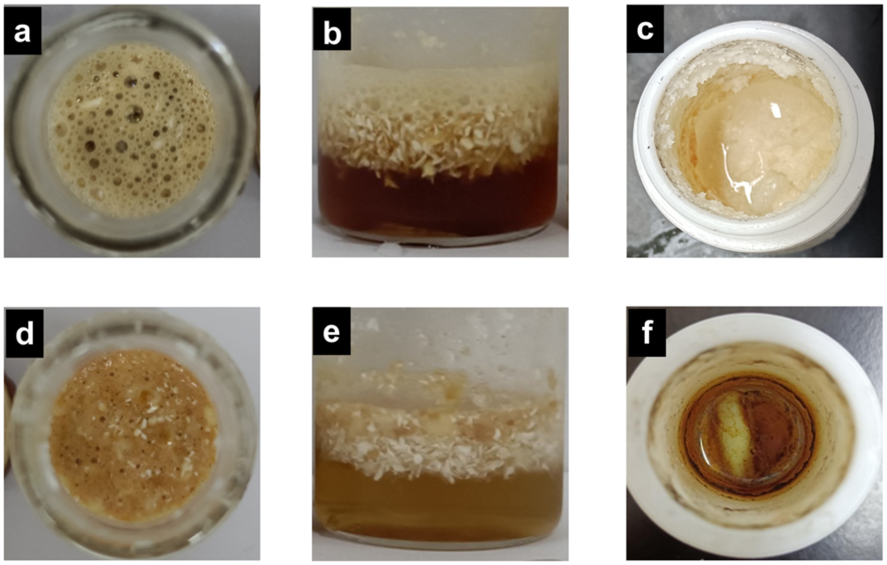


Fig. S7 The adsorption of PP to iron ions in H_2O_2 solution containing CTAB: top **(a)**, front **(b)**; The degradation of PP with the assistance of CTAB **(c)**. The adsorption of PP to iron ions in H_2O_2 solution containing SDS: top **(d)**, front **(e)**; The degradation of PP with the assistance of SDS **(f)**.

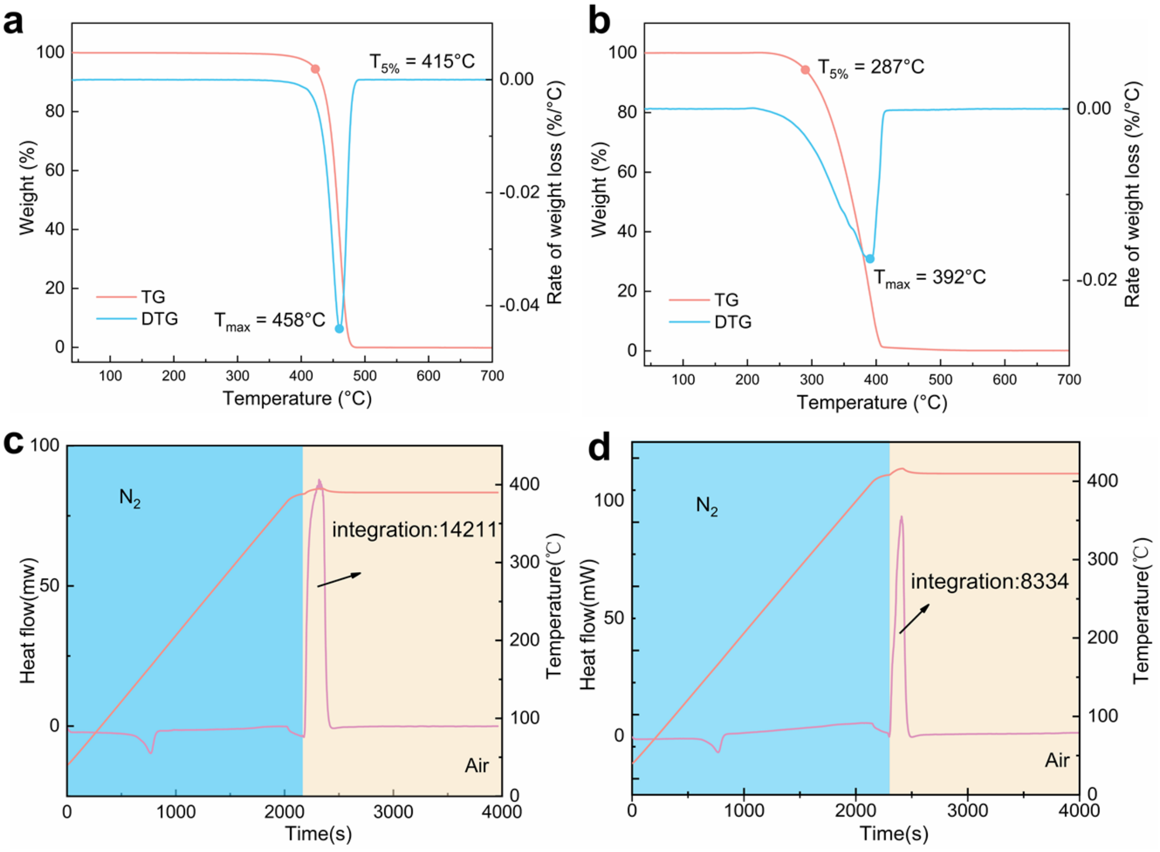


Fig. S8 Decomposition of PP (3 mg, with solvent treatment) from 40°C to 700°C under **(a)** N_2 atmosphere; **(b)** Air atmosphere. DSC of thermostatic decomposition of PP (5 mg, with solvent treatment) under air atmosphere at **(c)** 390°C; **(d)** 410°C.

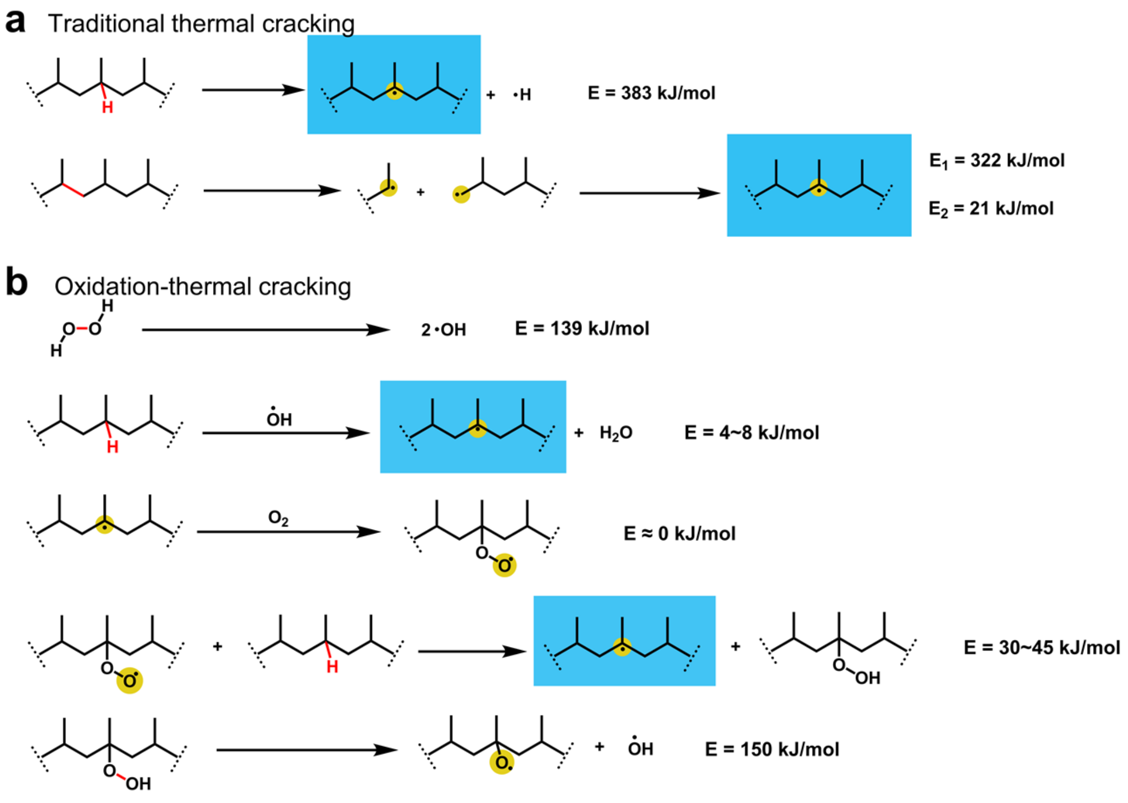


Fig. S9 Activation energy (*E*) required for generation of tertiary carbon-alkyl radicals by **(a)** traditional thermal cracking or **(b)** oxidative-thermal cracking without catalyst.

Table S1 PP was converted to DPP-THF and DPP-Xylene at different ratio of SDS to PP.

Entry	SDS:PP	DPP-THF					
		Yield (wt%)	Mw (10^3 Da)	PDI	Methyl ketone * (mmol/g)	Isopropenyl * (mmol/g)	Carboxyl † (mmol/g)
1	0.125	tace	-	-	-	-	-
2	0.30	53.5	1.97	1.94	0.92	0.40	1.42
3	0.35	58.8	1.79	1.89	1.03	0.40	1.02
4	0.40	60.0	1.56	1.95	1.29	0.56	1.26
5	0.45	57.2	1.74	2.00	1.11	0.50	1.42
6	0.50	50.5	1.78	1.74	0.80	0.50	1.20
7	0.875	23.1	2.02	1.97	0.68	0.17	0.81

*Calculated from ^{1}H NMR, using an internal standard. † Calculated by titration experiment using KOH ethanol solution.

Table S2 Oxygen contents in DPP-THF.

Entry	SDS:PP	Methyl ketone (mmol/g)	Carboxyl (mmol/g)	$O_{C=O}$% *	O_{COOH}% *	$O_{C=O}$% + O_{COOH}%	O_{EA}% †
1	0.30	0.92	1.42	1.47	4.54	6.02	6.63
2	0.35	1.03	1.02	1.65	3.26	4.91	6.63
3	0.40	1.29	1.26	2.07	4.03	6.10	6.51
4	0.45	1.11	1.42	1.78	4.54	6.32	7.42
5	0.50	0.80	1.20	1.27	3.84	5.11	7.15
6	0.875	0.68	0.81	1.09	2.59	3.68	3.61

* Calculated according to the corresponding group content. † Obtained by organic element analysis (EA).

Table S3 Benson group increments for oxidation cracking and thermal cracking of PP.

Group		$\Delta_f H_m^\theta$ (kJ/mol)	S_m^θ (J/mol)	Number of contributions to reaction		
				Methyl ketone	Carboxyl	Isopropenyl
G_1	CH_3-(C)	-42.19	127.29	0	0	-1
G_2	CH_2-(2C)	-20.64	39.43	-2	-1	-1
G_3	CH-(3C)	-7.95	-50.52	-1	-1	-2
G_4	CH_3-(CO)	-42.19	127.29	1	0	0
G_5	CH_2-(C,CO)	-21.77	40.18	1	1	0
G_6	CO-(2C)	-131.44	62.83	1	0	0
G_7	CO-(C,O)	-146.96	20.01	0	1	0
G_8	OH-(CO)	-243.25	102.66	0	1	0
G_9	CH_3-(=C)	-42.19	127.29	0	0	1
G_{10}	CH_2-(C,=C)	-19.92	41.02	0	0	1
G_{11}	$=CH_2$	26.2	115.57	0	0	1
G_{12}	=C-(2C)	43.28	-53.16	0	0	1
G_{13}	H_2O	-241.82	188.7	1	2	0
G_{14}	H_2O_2	-136.1	232.9	-1	-2	0