Quantifying the fragmentation of polypropylene upon exposure to accelerated weathering

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Experimental Section

Materials and Methods

Accelerated Weathering

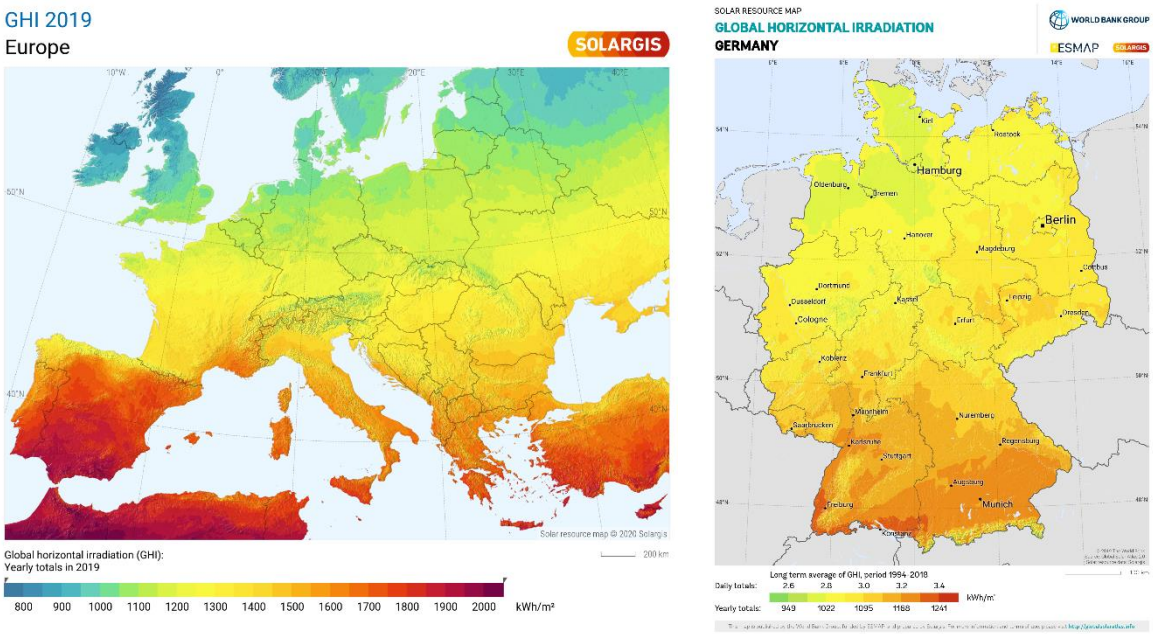


Figure S1. *Global horizontal irradiation for Europe and for Germany in kWh/m² for 2019. Source: SOLARGIS.*

Table S1. *Calculation of total irradiance in the Q-SUN Xe-3 chamber.*

Calculation of total irradiance in Q-SUN Xe-3 chamber		
Lamp settings*[1]	60	W/m²
Calculation factor*[2]	9.9	
Total irradiance in Q-SUN Xe-3 chamber	594	W/m²
Acceleration factor of Q-SUN Xe-3 chamber compared to Central Europe		
Solar irradiance per year*[3]	1000	kWh/m²
Hours per year	8765	h
Solar irradiance	114	W/m²
Acceleration factor of Q-SUN Xe-3 chamber*[4]	5.21	-

**[1] measured in the wavelength interval from 300 to 400 nm*
**[2] calculation factor converting the irradiance from 300 to 400 nm to the whole emission range of the Xenon lamp (300 – 800 nm). Extracted from Q-Sun Irradiance Conversion Sheet provided by Q-Lab Germany*
**[3] value was derived from Figure S1 for the longitude of Central Europe*
**[4] this value was calculated by division of the total irradiance in the Q-Sun Xe-3 chamber (594 W/m²) by the solar irradiance determined for Central Europe (114 W/m²)*

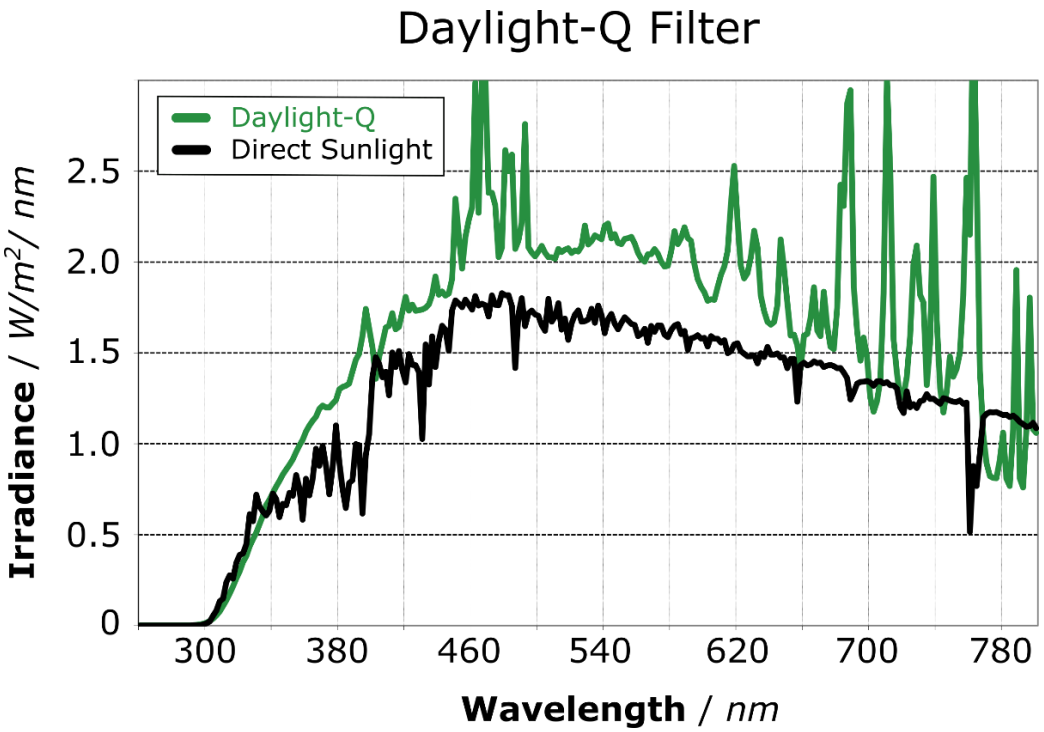
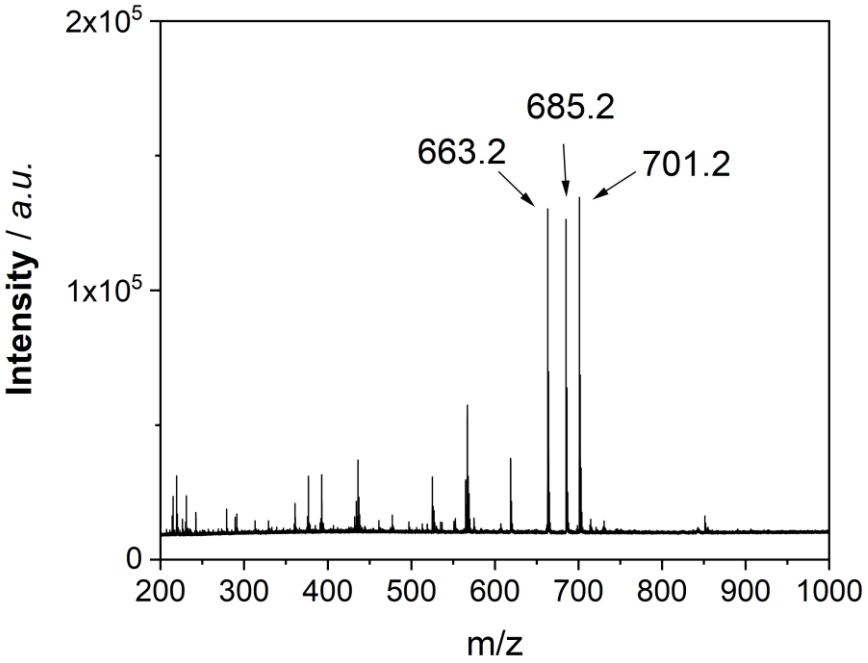


Figure S*2. Q-SUN daylight-Q filter compared to direct sunlight. Modified from Q-Lab Corporation, 2014, Technical Bulletin LX-5060, A Choice of Filters for Q-Sun Xenon Test Chambers.*

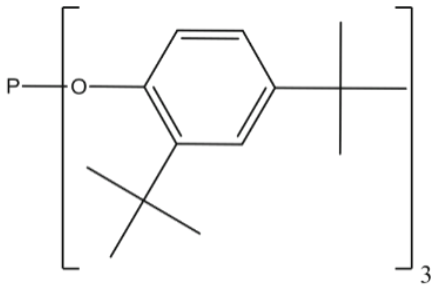
Results

Identification of the Processing Stabilizer via MALDI-TOF Mass Spectrometry

A



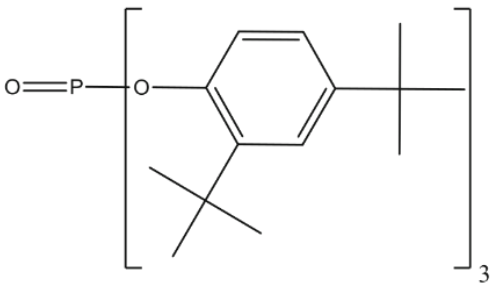
B Tris(2,4-di-tert-butylphenyl)phosphite
Irgafos® 168



$C_{42}H_{64}O_3P$

m/z = 647.5 $[M+H]^+$ (Fouyer et al., 2012; Schwarzinger et al., 2012)

C Tris(2,4-di-tert-butylphenyl)phosphate
Irgafos® 168, oxidized form



$C_{42}H_{64}O_4P$

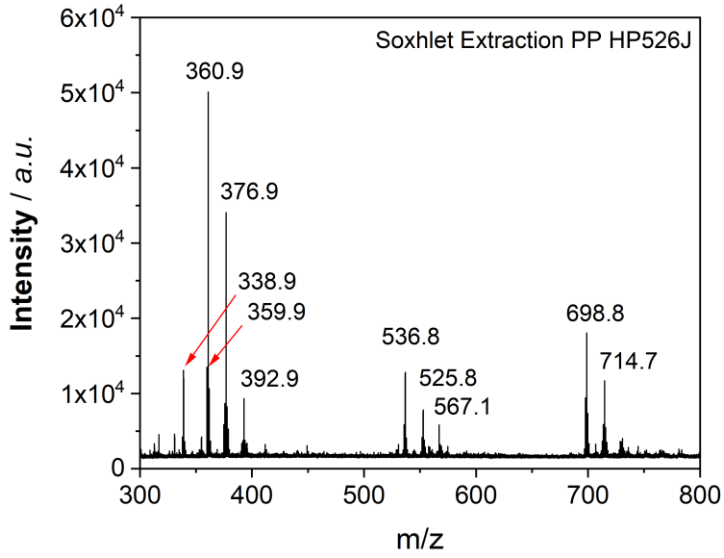
m/z = 663.5 $[M+H]^+$ (Fouyer et al., 2012; Schwarzinger et al., 2012)

m/z = 685.4 $[M+Na]^+$ (Schwarzinger et al., 2012)

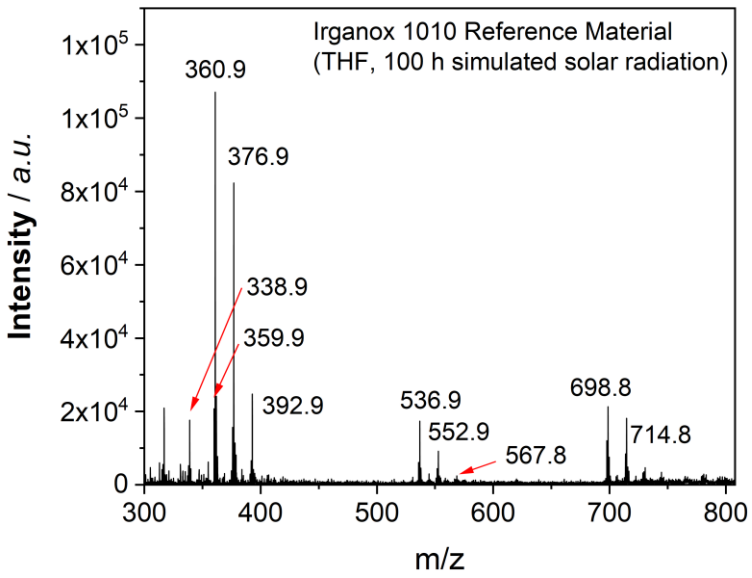
m/z = 701.4 $[M+K]^+$ (Schwarzinger et al., 2012)

Figure S3. (A) *MALDI spectrum of the first processing stabilizer in PP HP526 J. The three prominent peaks could be assigned to the oxidized species of Irgafos® 168 (Schwarzinger et al., 2012).* ***(B)*** *Chemical structure of Irgafos® 168 (Tris(2,4-di-tert-butylphenyl)phosphite) and* ***(C)*** *Tris(2,4-di-tert-butylphenyl)phosphate) together with m/z values from the literature.*

A



B



C

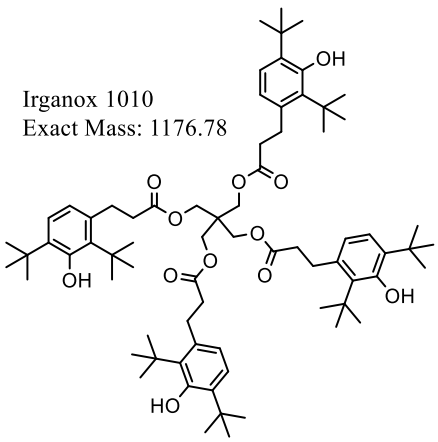


Figure S4. ***(A)*** *MALDI-TOF-MS spectrum of the second processing stabilizer in PP HP526 J. The prominent peaks are identical to those arising from Irganox® 1010 reference material, treated with simulated solar radiation in THF for 100 h in* ***(B)****. The structure of Irganox® 1010 is given in* ***(C)****.*

Identification of the processing stabilizers via ^{1}H, ^{13}C and ^{31}P liquid-state NMR spectroscopy

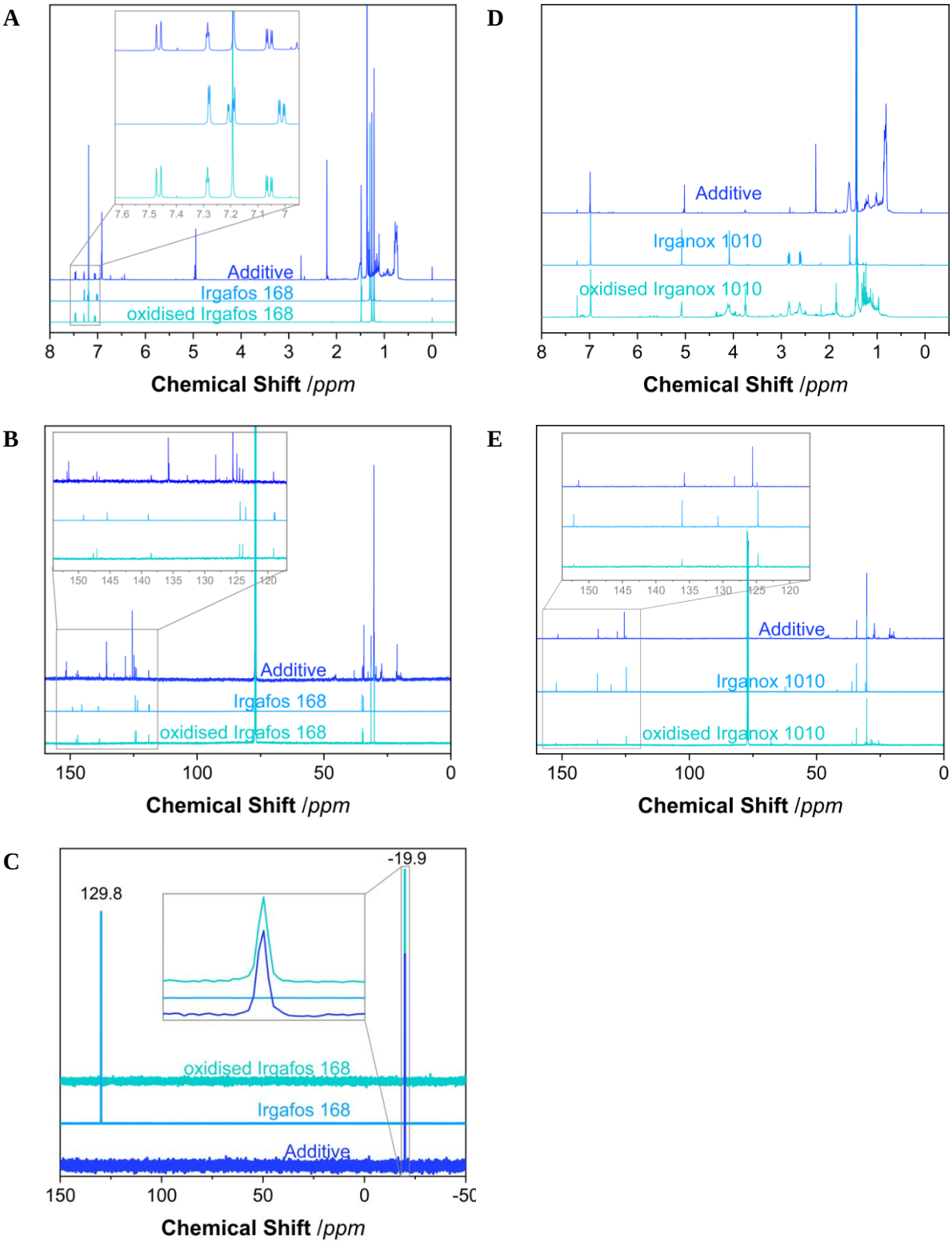


Figure S5. *Comparison of ^{1}H* ***(A)****, ^{13}C* ***(B)****, and ^{31}P* ***(C)*** *NMR spectra of the first extracted additive, tris(2,4-di-tert-butylphenyl)-phosphate and Irgafos® 168 as well as ^{1}H* ***(D)****, ^{13}C* ***(E)*** *spectra of the second extracted additive, Irganox® 1010 and Irganox® 1010 reference material, treated with simulated solar radiation in THF for 100 h. The ^{1}H and ^{13}C spectra were normalised to the proton and carbon resonances of tert-butyl groups and the ^{31}P spectra to the highest peak.*

Degradation Mechanisms

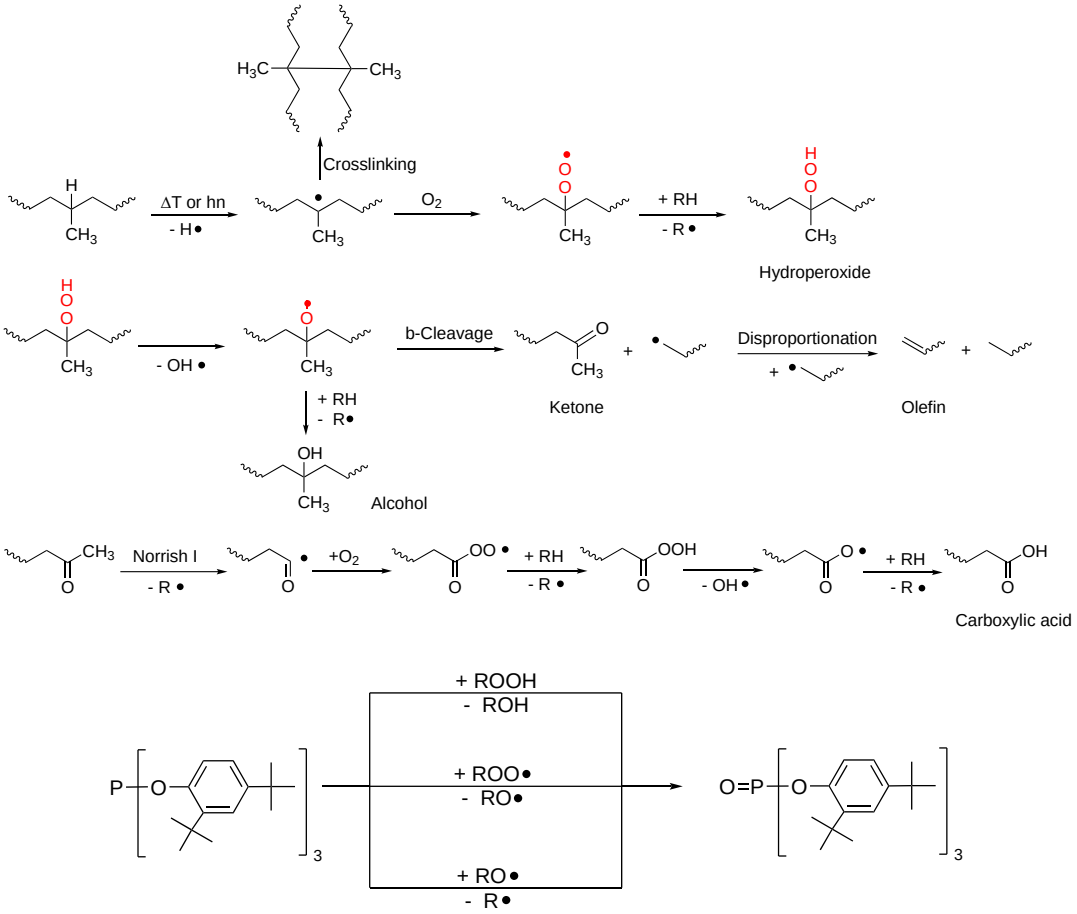


Figure S6. *Above: Scheme for the photooxidative degradation of PP explaining the formation of hydroperoxides, alcohols, ketones, olefins and carboxylic acids. Below: Reactions of the radical scavenger Irgafos® 168 with reactive hydroperoxides and peroxy- and alkoxy radicals. The reactive intermediates marked in red (above) are deactivated by the phosphite Irgafos® 168 which itself is oxidized to the phosphate (Maier and Schiller, 2016).*

Average Particle Size and Particle Size Distributions

Table S2. *Average particle sizes in µm for PP samples with and without stabilizer at exposure times from 0 h to 3200 h. Values display the average of three measurements.*

	With Stabilizer						**Without Stabilizer**
Exposure Time	**Average Particle Size**	**σ***	*Particle Volume*	*DMP Quantity*	*Surface Area*	*Total Surface Area (Quantity*Surface)*	**Average Particle Size**
hours	*µm*	*µm*	*µm³*	*counts*	*µm²*	*µm²*	*µm*
0	192.4	3.2	3705973		115812		119.4
24	197.0	1.9					119.7
50	189.9	3.1					121.6
100	197.5	3.6					108.8
150	199.7						-
200	200.1	3.1					85.4
250	197.4						-
300	193.4						-
350	187.0						-
400	148.1	0.8					53.6
450	98.5						-
500	68.2						-
550	51.8						-
600	41.3	0.9					31.4
800	16.5	0.04					22.2
1200	9.4	0.04					13.4
1600	5.6	0.01					8.6
2000	4.2	0.02					6.6
2400	4.1	0.04					5.8
2800	4.2	0.14					4.9
3200	4.1	0.21	36	102696	53	10^9	5.1

*σ is defined as the standard deviation of three independent measurements, from which the average particle size was calculated

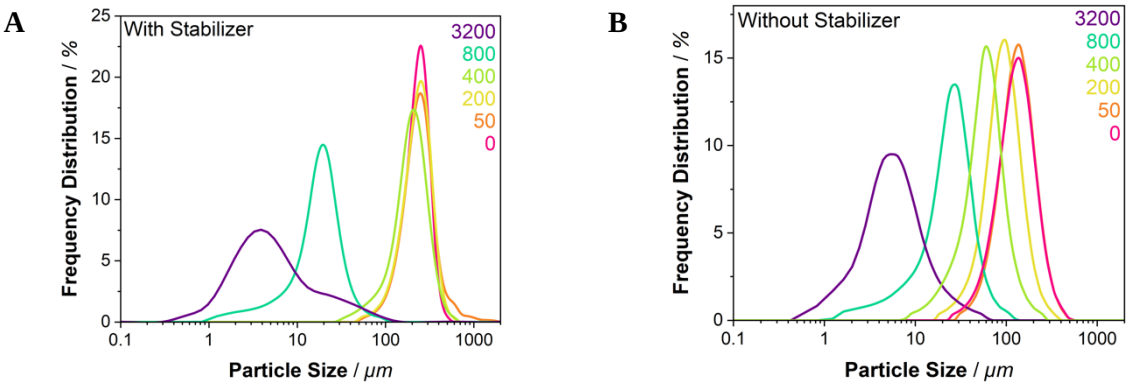


Figure S7. *Average particle size distributions for* ***(A)*** *PP with stabilizer and* ***(B)*** *PP particles without stabilizer.*

Molecular Weight Data

Table S3. *Number-average (M_n), weight-average (M_w), peak (M_p) molecular weights in g/mol, and dispersity (Đ) values for PP samples with and without stabilizer for different exposure times.*

	PP with stabilizer				PP without stabilizer			
Exposure Time	**M_n**	**M_w**	**M_p**	**Đ**	**M_n**	**M_w**	**M_p**	**Đ**
hours	*g/mol*	*g/mol*	*g/mol*		*g/mol*	*g/mol*	*g/mol*	
0	68300	795800	342000	11.7	68800	532000	256700	7.7
24	-	-	-	-	53500	293700	174000	5.5
50	75000	739700	328200	9.9	13000	47700	41300	3.7
100	63400	698600	296200	11.0	5400	17200	13700	3.2
150	44900	731200	328200	16.3	-	-	-	-
200	35100	669100	296200	19.1	3300	8800	7500	2.7
250	64600	661800	296200	10.2	-	-	-	-
300	30000	162700	93900	5.4	-	-	-	-
350	10400	40300	31500	3.9	-	-	-	-
400	5000	16100	10900	3.2	2100	4500	4000	2.1
450	3500	9300	7600	2.7	-	-	-	-
500	3000	6500	4100	2.2	-	-	-	-
550	2500	5000	3800	2.0	-	-	-	-
600	2400	4400	3700	1.9	1800	3400	2000	1.9
800	1900	3500	2200	1.8	1500	2700	1900	1.8
1200	1600	2600	1900	1.7	1200	2000	1600	1.7
1600	1300	2200	1700	1.6	1100	1700	1500	1.6
2000	1300	1900	1600	1.5	1000	1500	1300	1.6
2400	1100	1700	1500	1.6	800	1400	1200	1.7
2800	900	1600	1300	1.7	800	1200	1200	1.7
3200	1000	1500	1300	1.6	700	1200	1000	1.7

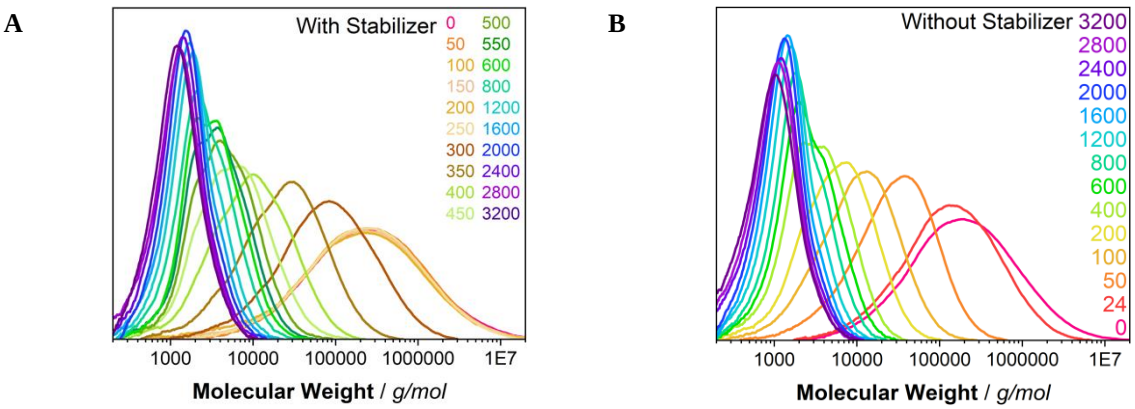


Figure S8. *Molecular weight distributions in g/mol of* ***(A)*** *PP with stabilizer and* ***(B)*** *PP without stabilizer for exposure time intervals from 0 h to 3200 h.*

Crystallinity and Melting Temperature

Table S4. *Crystallinity and melting temperature measurements for PP with stabilizer and PP without stabilizer.*

	PP with stabilizer		PP without Stabilizer	
Exposure Time	**Crystallinity χc**	**Melting Temp. T_m**	**Crystallinity χc**	**Melting Temp. T_m**
hours	*%*	*°C*	*%*	*°C*
0	52.1	164.8	45.1	164.7
24	49.7	164.6	52.5	164.8
50	49.6	164.4	54.0	163.6
100	48.0	164.7	52.7	157.7
200	51.0	164.6	61.6	152.6
350	48.7	162.4	-	-
400	64.6	156.1	61.3	150.0
600	65.7	148.5	58.4	147.2
800	67.7	145.8	63.4	145.0
1200	63.0	142.2	61.0	143.0
1600	62.2	137.8	58.8	141.0
2000	59.50	135.8	57.1	136.1
2400	57.9	130.9	59.8	133.4
2800	48.0	122.9	57.8	131.2
3200	51.3	119.5	63.0	125.3

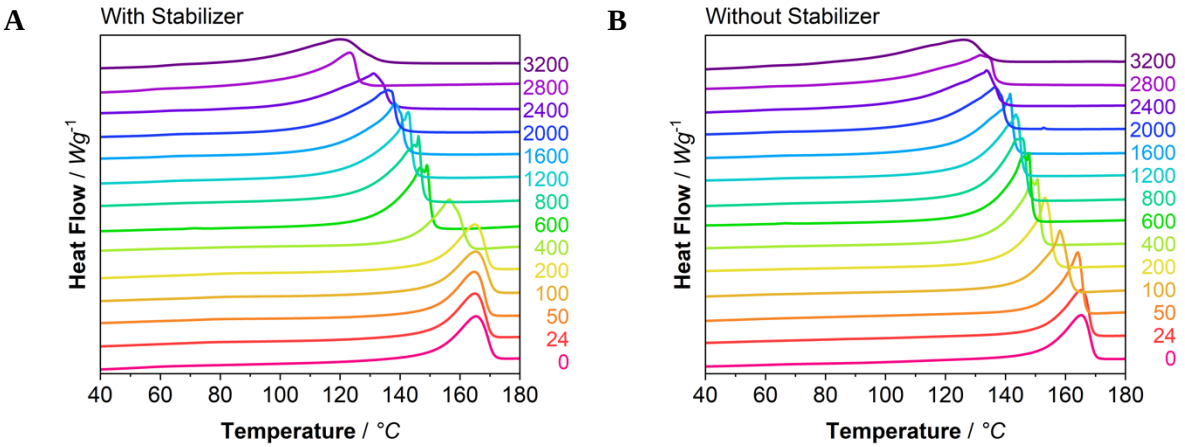


Figure S9. *DSC measurements. Heat flow in W/g vs. temperature in °C for* ***(A)*** *PP particles with stabilizer and* ***(B)*** *PP particles without stabilizer.*

Evaluation of Crystallinity via ^{13}C CP MAS NMR Spectroscopy

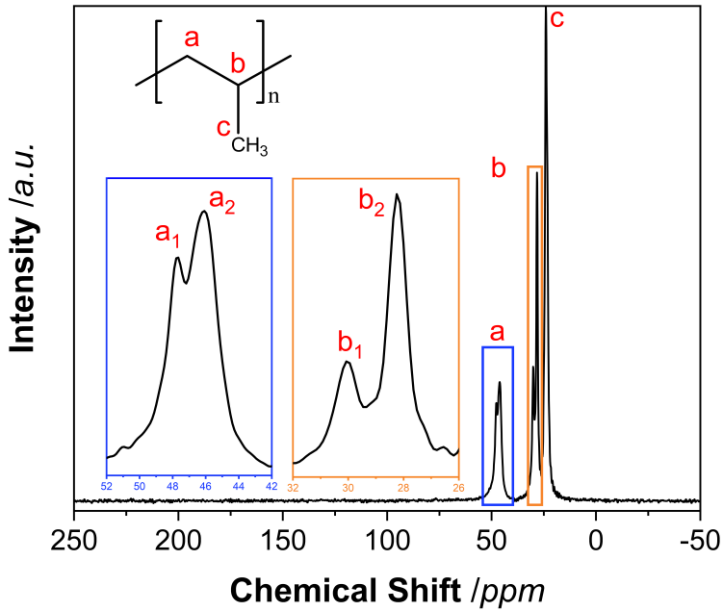


Figure S10. *^{13}C CP MAS NMR spectrum of the PP particles with stabilizer prior to weathering with signal assignment. In the enlarged PP spectra (blue and orange rectangle) the differences of the resonances of the amorphous (signal a1 and b1) and crystalline (signal a2 and b2) phase become visible (Hronský et al., 2014).*

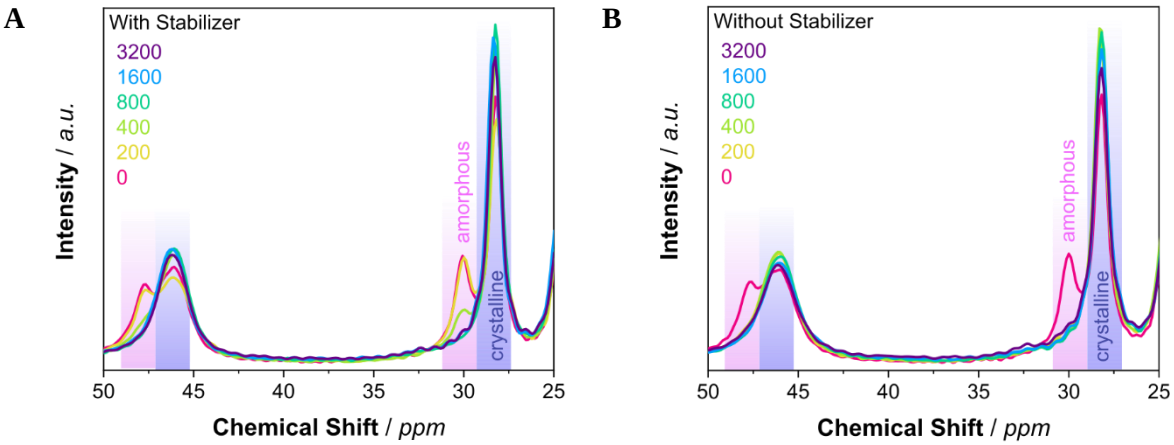


Figure S11. *^{13}C CP MAS NMR spectra of the PP particles with **(A)** and without **(B)** stabilizer for 0, 400 and 3200 h weathering time. Upon irradiation, a shift of signal intensity from the amorphous phase resonances (30 ppm, 48 ppm) to the crystalline phase resonances (28 ppm, 46 ppm) is observed (Hronský et al., 2014). The spectra are normalised to the integral of the backbone signal (35-20 ppm and 55-35 ppm).*

Calculation of Defect Proportions via ^{13}C CP MAS NMR Spectroscopy

Table S5. *Refinement parameters for the ^{13}C CP NMR spectra of weathered PP samples with and without stabilizer. Refinements were carried out with pseudo-Voigt lineshapes (Eq. 1) where δ_{iso} is the isotropic chemical shift, LB the line broadening, x the Gauss/Lorentz ratio and I the relative intensity. The latter is given in percent as fraction of the total spectral intensity. Refinement parameters marked in grey were obtained by simultaneous free refinements of defect peaks in the two spectra with longest weathering times and were kept constant in the subsequent refinements.*

$$f(\delta) = I \cdot [(1-x)\frac{2\,LB}{4\pi\cdot(\delta-\delta_{iso})^2+\pi\cdot LB^2} + x \cdot \frac{\sqrt{4\ln(2)}}{\sqrt{\pi}\,LB} \cdot e^{-\frac{4\ln(2)}{LB^2}(\delta-\delta_{iso})^2}] \quad \text{(Eq. 1)}$$

Spectrum	Peak Assignment	δ_{iso} [ppm]	LB [ppm]	x	Intensity [%]
PP with stabilizer 3200 h	Ketone	216	29.8	0.5	1.1
	Carboxylic acid	179.8	11.9	0.9	1.3
	Peroxide	86.8	8.8	0.2	1.6
	Alcohol	75.6	8.8	0.2	2.2
	CH_2	46.4	2.6	0.0	17.8
		50.1	10.0	0.0	3.0
	CH	28.5	1.5	0.0	19.2
		29.7	4.9	0.0	6.2
	CH_3	23.9	2.3	0.3	41.6
		19.6	7.2	0.2	4.1
PP with stabilizer 2800 h	Ketone	216	29.8	0.5	1.4
	Carboxylic acid	179.8	11.9	0.9	1.2
	Peroxide	86.8	8.8	0.2	2.0
	Alcohol	75.6	8.8	0.2	2.2
	CH_2	46.5	2.6	0.0	18.6
		50.6	11.6	0.0	4.0
	CH	28.6	1.5	0.0	19.8
		29.9	5.3	0.0	7.8
	CH_3	24.1	2.3	0.4	41.3
		19.4	5.8	1.0	1.6
PP with stabilizer 2400 h	Ketone	216	29.8	0.5	1.0
	Carboxylic acid	179.8	11.9	0.9	1.0
	Peroxide	86.8	8.8	0.2	1.7
	Alcohol	75.6	8.8	0.2	2.0
	CH_2	46.5	2.6	0.0	18.4
		51.0	11.4	0.0	3.7
	CH	28.5	1.5	0.0	21.9
		30.1	5.9	0.0	5.3
	CH_3	24.1	2.3	0.4	41.0
		20.7	7.1	0.5	4.2
PP with stabilizer 2000 h	Ketone	216	29.8	0.5	1.1
	Carboxylic acid	179.8	11.9	0.9	1.2
	Peroxide	86.8	8.8	0.2	1.7
	Alcohol	75.6	8.8	0.2	1.8
	CH_2	46.5	2.6	0.0	19.1
		50.4	11.3	0.0	3.5
	CH	28.5	1.5	0.0	20.9
		29.9	5.4	0.0	6.8
	CH_3	24.0	2.3	0.4	42.3
		19.4	5.7	1.0	1.5

Spectrum	Peak Assignment	δ_{iso} [ppm]	LB [ppm]	x	Intensity [%]
PP with stabilizer 1600 h	Ketone	216	29.8	0.5	0.7
	Carboxylic acid	179.8	11.9	0.9	1.0
	Peroxide	86.8	8.8	0.2	1.6
	Alcohol	75.6	8.8	0.2	1.7
	CH_2	46.5	2.5	0.0	18.8
		50.4	10.8	0.0	4.0
	CH	28.5	1.6	0.0	24.1
		31.5	4.8	0.0	3.4
	CH_3	24.0	2.3	0.4	42.2
		20.5	7.5	0.9	2.5
PP with stabilizer 1200 h	Ketone	216	29.8	0.5	0.8
	Carboxylic acid	179.8	11.9	0.9	0.7
	Peroxide	86.8	8.8	0.2	1.4
	Alcohol	75.6	8.8	0.2	1.3
	CH_2	46.3	2.6	0.0	20.6
		50.9	9.8	0.0	3.1
	CH	28.4	1.4	0.0	20.2
		29.4	4.0	0.0	6.6
	CH_3	24.0	2.2	0.3	44.6
		18.1	5.9	1.0	0.6
PP with stabilizer 800 h	Ketone	216	29.8	0.5	0.7
	Carboxylic acid	179.8	11.9	0.9	0.5
	Peroxide	86.8	8.8	0.2	1.4
	Alcohol	75.6	8.8	0.2	0.8
	CH_2	46.3	2.5	0.0	19.2
		50.6	10.3	0.0	3.3
	CH	28.4	1.5	0.0	22.8
		30.3	5.3	0.0	4.1
	CH_3	23.9	2.3	0.3	45.0
		19.7	7.1	0.4	2.1
PP with stabilizer 600 h	Ketone	216	29.8	0.5	0.0
	Carboxylic acid	179.8	11.9	0.9	0.0
	Peroxide	86.8	8.8	0.2	0.9
	Alcohol	75.6	8.8	0.2	0.8
	CH_2	46.2	2.8	0.4	16.0
		48.0	8.7	0.0	8.6
	CH	28.3	1.5	0.0	21.6
		29.5	5.7	0.8	7.0
	CH_3	23.8	2.3	0.4	43.5
		19.1	6.0	1.0	1.4
PP with stabilizer 400 h	Ketone	216	29.8	0.5	0.0
	Carboxylic acid	179.8	11.9	0.9	0.0
	Peroxide	86.8	8.8	0.2	0.5
	Alcohol	75.6	8.8	0.2	0.4
	CH_2	46.4	2.6	0.0	18.9
		48.5	3.7	0.0	3.3
	CH	28.4	1.5	0.0	20.3
		29.8	4.2	1.0	5.6
	CH_3	23.9	2.2	0.4	45.7
		21.4	7.8	0.0	5.2

Spectrum	Peak Assignment	δ_{iso} [ppm]	LB [ppm]	x	Intensity [%]
PP with stabilizer 200 h	Ketone	216	29.8	0.5	0.0
	Carboxylic acid	179.8	11.9	0.9	0.0
	Peroxide	86.8	8.8	0.2	0.0
	Alcohol	75.6	8.8	0.2	0.0
	CH_2	44.1	2.8	0.0	14.6
		45.9	2.5	0.0	8.1
	CH	26.4	1.6	0.0	18.4
		28.2	1.9	0.0	9.9
	CH_3	22.0	2.1	0.3	41.8
		19.8	8.5	0.0	7.2
PP with stabilizer 0 h	Ketone	216	29.8	0.5	0.0
	Carboxylic acid	179.8	11.9	0.9	0.0
	Peroxide	86.8	8.8	0.2	0.0
	Alcohol	75.6	8.8	0.2	0.0
	CH_2	46.3	2.5	0.6	9.9
		47.9	3.7	0.0	14.3
	CH	28.4	1.5	0.0	18.2
		30.3	1.9	0.0	9.9
	CH_3	24.0	2.1	0.2	44.5
		24.4	1.1	0.2	3.2
PP without stabilizer 3200 h	Ketone	214	29.8	0.5	1.3
	Carboxylic acid	178.7	11.9	0.9	1.1
	Peroxide	84.6	8.8	0.2	2.0
	Alcohol	74.0	8.8	0.2	2.2
	CH_2	44.4	3.1	0.0	18.1
		48.5	14.4	0.0	4.0
	CH	26.5	1.6	0.0	18.0
		27.1	5.2	0.0	9.7
	CH_3	22.0	2.3	0.4	35.4
		18.1	8.2	0.0	6.0
PP without stabilizer 2800 h	Ketone	214	29.8	0.5	1.6
	Carboxylic acid	178.7	11.9	0.9	1.2
	Peroxide	84.6	8.8	0.2	2.1
	Alcohol	74.0	8.8	0.2	2.0
	CH_2	44.4	3.1	0.0	18.6
		49.6	12.4	0.0	3.1
	CH	26.5	1.6	0.0	19.8
		27.2	5.6	0.0	8.4
	CH_3	21.9	2.3	0.5	33.8
		19.0	7.5	0.0	7.7
PP without stabilizer 2400 h	Ketone	214	29.8	0.5	0.9
	Carboxylic acid	178.7	11.9	0.9	0.9
	Peroxide	84.6	8.8	0.2	1.9
	Alcohol	74.0	8.8	0.2	2.0
	CH_2	44.4	3.1	0.0	18.9
		49.8	15.3	0.0	4.2
	CH	26.5	1.5	0.0	18.7
		27.1	4.9	0.0	9.2
	CH_3	22.0	2.3	0.4	36.7
		18.1	7.2	0.0	5.2

Spectrum	Peak Assignment	δ_{iso} [ppm]	LB [ppm]	x	Intensity [%]
PP without stabilizer 2000 h	Ketone	214	29.8	0.5	1.1
	Carboxylic acid	178.7	11.9	0.9	0.9
	Peroxide	84.6	8.8	0.2	1.4
	Alcohol	74.0	8.8	0.2	1.5
	CH_2	44.3	3.0	0.1	18.1
		48.0	6.7	0.0	1.9
	CH	26.4	1.6	0.2	19.9
		27.7	4.3	0.0	4.2
	CH_3	22.0	2.3	0.3	37.9
		20.0	11.9	0.0	12.4
PP without stabilizer 1600 h	Ketone	214	29.8	0.5	1.2
	Carboxylic acid	178.7	11.9	0.9	0.8
	Peroxide	84.6	8.8	0.2	1.7
	Alcohol	74.0	8.8	0.2	1.5
	CH_2	44.3	3.0	0.2	17.0
		47.2	9.9	0.0	4.0
	CH	26.4	1.6	0.2	19.5
		27.3	6.1	0.7	5.0
	CH_3	21.9	2.3	0.4	35.2
		20.2	9.6	0.0	13.3
PP without stabilizer 1200 h	Ketone	214	29.8	0.5	0.6
	Carboxylic acid	178.7	11.9	0.9	0.5
	Peroxide	84.6	8.8	0.2	1.1
	Alcohol	74.0	8.8	0.2	1.1
	CH_2	44.2	3.0	0.0	19.9
		49.1	6.1	0.0	0.7
	CH	26.5	1.6	0.0	23.4
		28.1	5.8	1.0	2.2
	CH_3	11.7	18.9	0.4	2.1
		-16.8	53.8	0.1	1.9
		21.9	2.3	0.4	38.3
		19.3	6.6	0.0	7.6
PP without stabilizer 800 h	Ketone	214	29.8	0.5	0.6
	Carboxylic acid	178.7	11.9	0.9	0.2
	Peroxide	84.6	8.8	0.2	1.0
	Alcohol	74.0	8.8	0.2	1.0
	CH_2	44.3	3.0	0.2	18.5
		48.0	6.7	0.0	2.6
	CH	26.5	1.7	0.0	24.9
		29.5	3.6	1.0	1.1
	CH_3	-7.6	49.1	0.4	2.1
		21.9	2.3	0.4	38.2
		19.4	9.2	0.0	9.3

Spectrum	Peak Assignment	δ_{iso} [ppm]	LB [ppm]	x	Intensity [%]
PP without stabilizer 600 h	Ketone	214	29.8	0.5	0.5
	Carboxylic acid	178.7	11.9	0.9	0.5
	Peroxide	84.6	8.8	0.2	0.9
	Alcohol	74.0	8.8	0.2	0.6
	CH_2	44.4	3.0	0.1	20.0
		48.8	4.1	0.3	1.1
	CH	26.5	1.7	0.5	19.2
		28.0	4.4	0.9	4.3
	CH_3	0.5	49.5	1.0	2.5
		22.1	2.4	0.3	42.1
		19.3	9.7	0.0	7.9
PP without stabilizer 400 h	Ketone	214	29.8	0.5	0.4
	Carboxylic acid	178.7	11.9	0.9	0.4
	Peroxide	84.6	8.8	0.2	0.9
	Alcohol	74.0	8.8	0.2	0.6
	CH_2	44.4	2.9	0.2	19.5
		48.5	6.9	0.0	2.8
	CH	26.5	1.6	0.4	20.1
		27.4	6.2	1.0	5.4
	CH_3	1.2	50.7	0.0	1.7
		22.1	2.3	0.3	41.5
		19.2	9.6	0.0	6.2
PP without stabilizer 200 h	Ketone	214	29.8	0.5	0.4
	Carboxylic acid	178.7	11.9	0.9	0.3
	Peroxide	84.6	8.8	0.2	0.8
	Alcohol	74.0	8.8	0.2	0.6
	CH_2	44.4	2.9	0.3	18.6
		47.9	5.4	0.0	3.1
	CH	26.5	1.7	0.2	23.6
		29.0	3.9	1.0	1.9
	CH_3	-0.7	38.8	0.8	1.3
		22.1	2.3	0.3	42.3
		19.9	9.6	0.0	6.5
PP without stabilizer 0 h	Ketone	214	29.8	0.5	0.0
	Carboxylic acid	178.7	11.9	0.9	0.0
	Peroxide	84.6	8.8	0.2	0.0
	Alcohol	74.0	8.8	0.2	0.0
	CH_2	44.1	2.6	0.5	10.4
		46.0	3.0	0.0	13.0
	CH	26.4	1.6	0.2	17.4
		28.3	1.9	0.0	10.1
	CH_3	-0.7	49.5	0.2	2.5
		22.1	2.0	0.3	38.7
		21.4	5.5	0.0	7.9

Table S6. *Correction factors for PP with and without stabilizer determined with quantitative multi-CP spectra of the respective 3200 h weathered sample. Used to calibrate the defect intensities in the CP spectra (Meides et al., 2021).*

Functional Group	**PP with stabilizer**	**PP without stabilizer**
	c_i 3200 h	**c_i 3200 h**
Ketone	0.49	0.50
Carboxylic acid	0.85	0.84
Peroxide	0.76	0.74
Alcohol	0.80	0.77

$$\rho_{ru} = [1 - (3 \cdot I_{ketone}) - (2 \cdot I_{COOH}) - (3 \cdot I_{POOH}) - (3 \cdot I_{OH})] / 3 \quad \text{(Eq. 2)}$$

with:

ρ_{ru}	proportion of propylene RUs relative to the proportion of defects
I_{ketone}	relative intensity of the ketone resonance
I_{COOH}	relative intensity of the carboxylic acid resonance
I_{POOH}	relative intensity of the peroxide resonance
I_{OH}	relative intensity of the alcohol resonance.

Since the ratio of the different groups is $I_{ketone} : I_{COOH} : I_{POOH} : I_{OH} : p_{ru}$, the absolute proportions of the carbonyl groups (ap_{ketone}), carboxy groups (ap_{COOH}), peroxy groups (ap_{POOH}) and hydroxy groups (ap_{POH}) can be calculated once ρ_{ru} is known:

$$ap_{ketone} = I_{ketone} / (p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH}) \quad \text{(Eq. 3)}$$

$$ap_{COOH} = I_{COOH} / (p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH}) \quad \text{(Eq. 4)}$$

$$ap_{POOH} = I_{POOH} / (p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH}) \quad \text{(Eq. 5)}$$

$$ap_{OH} = I_{OH} / (p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH}) \quad \text{(Eq. 6)}$$

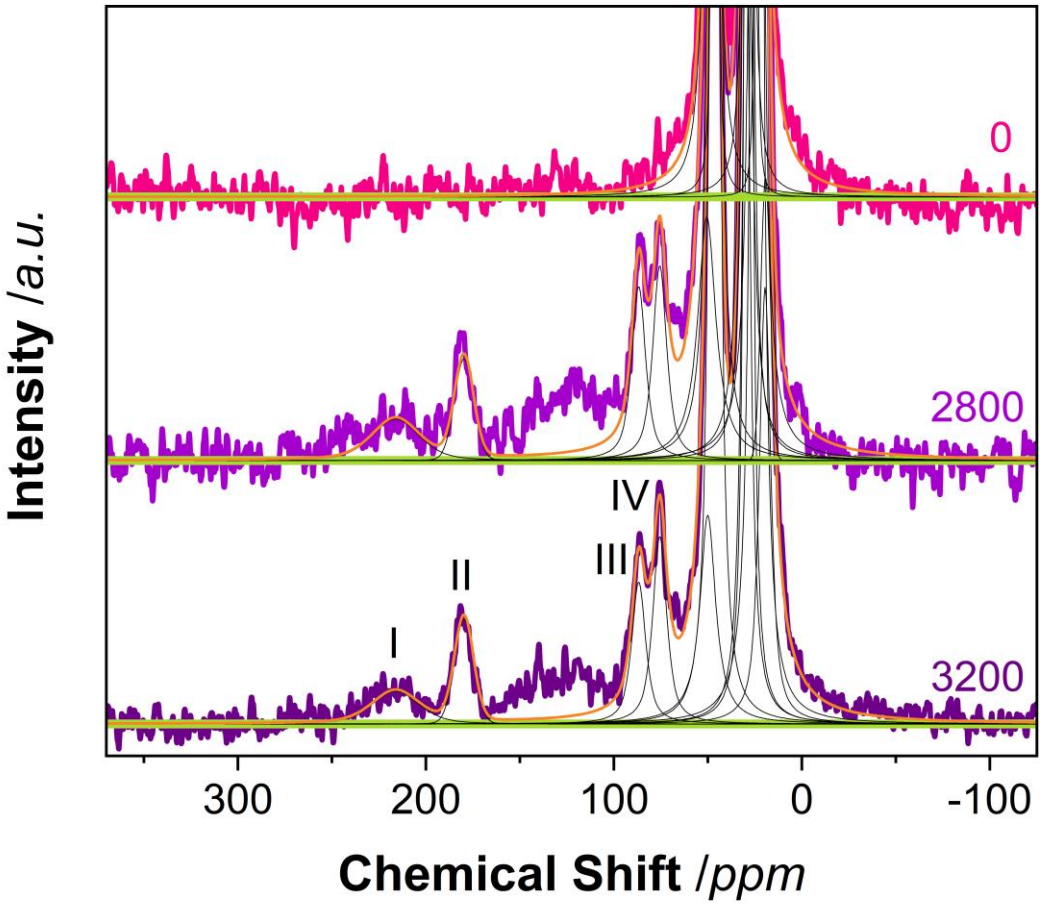


Figure S12. *^{13}C CP MAS NMR spectra of the PP particles with stabilizer for 0, 2800 and 3200 h weathering time. The spectra are normalised to the intensity of the methyl sidechain carbon signal (at approx. 24 ppm). Individual spectra are shifted vertically for better comparability. Additionally, the baselines (green), individual refinements for the peaks (black) and the cumulative lineshape (orange) are shown in the spectra. No refinement of vinylidenes was performed between 100 – 150 ppm since the resonances of the decomposition products of Irgafos® 168 superimpose with the vinylidene resonances.*

SEM Images

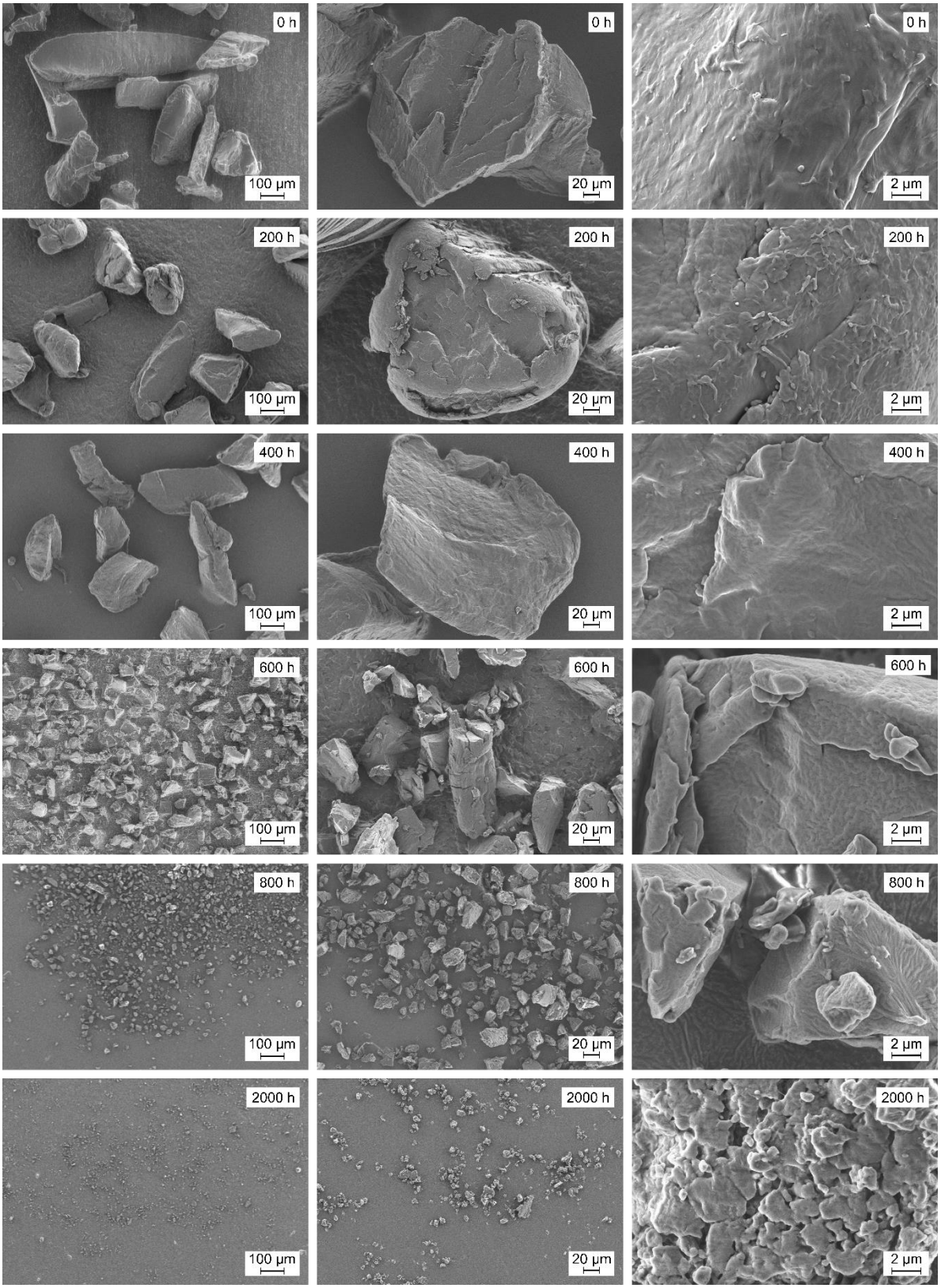


Figure S13. *SEM images of PP with stabilizer after irradiation for different time intervals.*

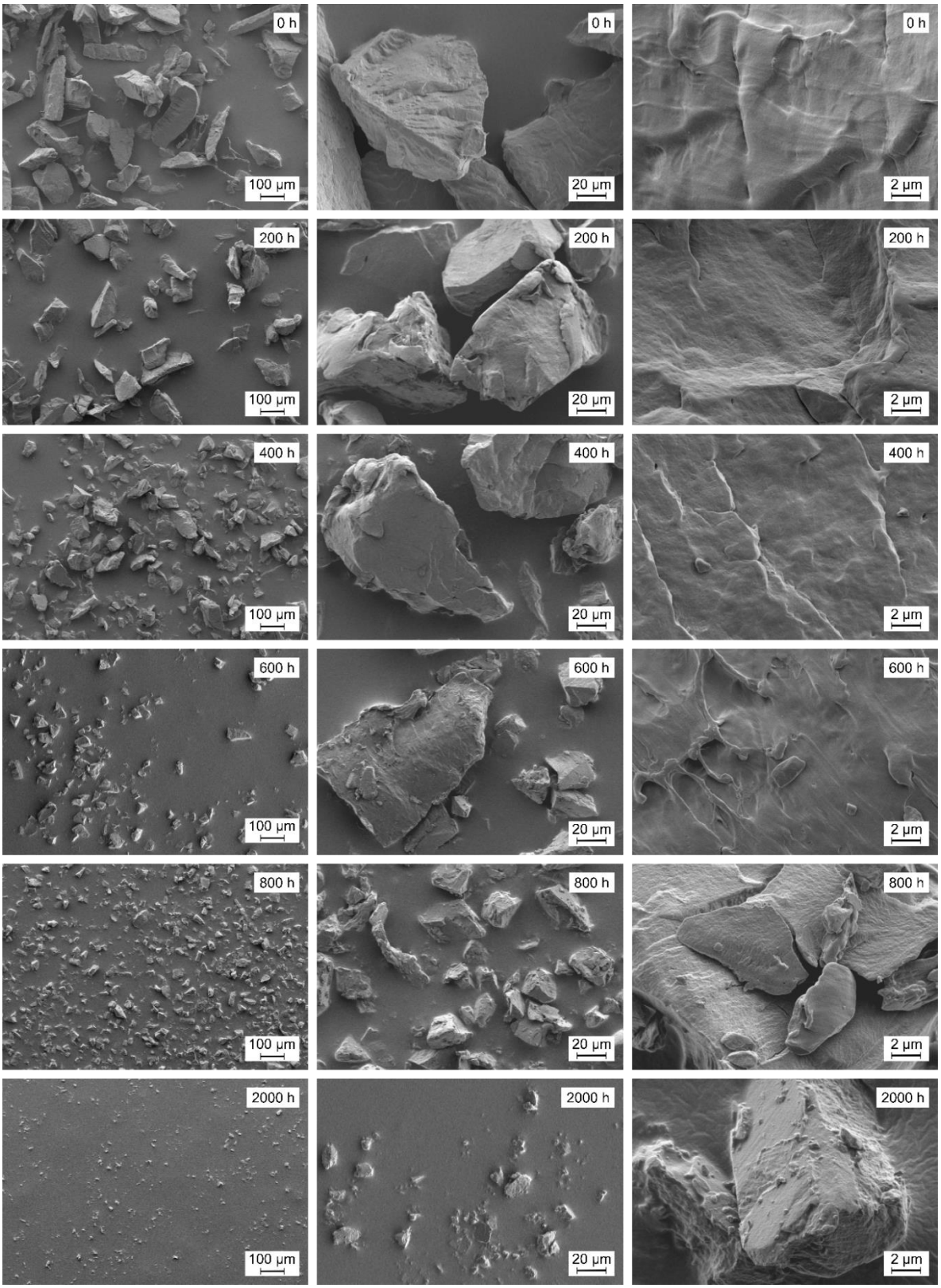


Figure S14. *SEM images of PP without stabilizer after irradiation for different time intervals.*

Supplementary References

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