Supporting Information

for

Quantification of photooxidative defects in weathered microplastics using $^{13}$C multiCP NMR spectroscopy

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S1 Figures and tables

**Synthesis of $^{13}$C labelled polystyrene**

Fig. S1 Synthesis of polystyrene from a 4:1 mixture of $^{13}$C labelled and non-labelled styrene with radical initiator AIBN.

Table S1 Educt proportions for PS-$^{13}$C synthesis sketched in Fig. S1.

| Substance          | n [mmol] | Equivalents | m [g]  | M [g/mol] | V [mL] | $\rho$ [g/mL] |
|--------------------|----------|-------------|--------|-----------|--------|--------------|
| Styrene            | 38.04    | 0.8         | 3.96   | 104.15    | 4.4    | 0.91         |
| $^{13}$C enriched Styrene | 9.51    | 0.2         | 1      | 105.14    | 1.1    | 0.92         |
| AIBN               | 0.476    | 0.01        | 0.0677 | 142.25    | /      | /            |
Accelerated weathering

Fig. S2 Radiation spectrum of the weathering chamber created by three Xe lamps and a Q-SUN daylight-Q filter compared to the one of direct sunlight. Taken and modified from Q-Lab Corporation, 2014, Technical Bulletin LX-5060, A Choice of Filters for Q-Sun Xenon Test Chambers.

Fig. S3 Global horizontal irradiation for Europe and for Germany in kWh/m² for 2019. Source: SOLARGIS.
**Table S2** Calculation of total irradiance in the Q-SUN Xe-3 weathering chamber as well as the acceleration factor for Central Europe.

| Calculation of total irradiance in Q-SUN Xe-3 chamber |          |          |
|-------------------------------------------------------|----------|----------|
| Calculation factor\(^*1\)                            | 9.9      | -        |
| Lamp settings                                         | 60       | W/m\(^2\) |
| Total irradiance in Q-SUN Xe-3 chamber                | 594      | W/m\(^2\) |

| Acceleration factor of Q-SUN Xe-3 chamber compared to Central Europe |
|---------------------------------------------------------------------|
| Solar irradiance per year\(^*2\)                                    | 1000     | kWh/m\(^2\) |
| Hours per year                                                      | 8765     | h          |
| Solar irradiance                                                    | 114      | W/m\(^2\)  |
| Acceleration factor of Q-SUN Xe-3 chamber\(^*3\)                   | 5.21     | -          |

\(^*1\) calculation factor extracted from Q-Sun Irradiance Conversion Sheet provided by Q-Lab Germany  
\(^*2\) value was derived from Figure S3 for the longitude of Central Europe  
\(^*3\) this value was calculated by division of the total irradiance in the Q-Sun Xe-3 chamber (594 W/m\(^2\)) by the solar irradiance determined for Central Europe (114 W/m\(^2\))
Degradation Mechanism

Fig. S4 Typical pathways for photooxidative degradation of PS, outlining the formation of hydroperoxides, alcohols, in-chain and end-chain ketones, carboxylic acids, esters, hemiketals and ketals (see main paper refs. 18, 36, 39 and 61).
NMR Spectroscopy

Fig. S5 MultiCP sequence as introduced in ref. 52 used for this work.

Fig. S6 Comparison of $^{13}$C CP MAS NMR spectra of PS-$^{13}$C (black) and PS in natural abundance (red) of the particle samples weathered for 2400 h. Both spectra are normalised to the intensity of the ipso carbon resonance at 149 ppm.

Fig. S7 $^{13}$C CP MAS spectra of PS-$^{13}$C weathered for 2400 h highlighting the spectral range for ketone and carboxy functions for selected CP build-up times (400 μs to 4000 μs). The ketone resonance (a) is split in in-chain (left shoulder, (a), 204 ppm) and end-chain ketones ((a’), 197 ppm). The peak at 172 ppm is attributed to the carboxylic acids (b), the small shoulder at 166 ppm to esters (b’). The relative intensity ratios of the shoulders and the main peaks do not change significantly with the polarization time. The dashed lines represent pseudo-Voigt fits of the individual resonances.
**Fig S8** $^{13}$C multiCP MAS spectra of PS-$^{13}$C weathered for 2400 h, measured with a block length of 150 μs, different number of blocks $n$ (13 or 20) and waiting times $t_w$ (2 s or 3 s). The intensities of all spectra are normalized to the intensity of the aliphatic CH/CH$_2$ resonance. The shape and intensity of the individual resonances are practically independent of the varied measurement parameters.

**Fig. S9** Comparison of $^{13}$C CP ($\tau_{CP} = 2$ ms; black line) and multiCP $^{13}$C ($\tau_{block} = 250$ μs with 12 blocks and $\tau_{CP}^{tot} = 3$ ms; red line) MAS NMR spectra for PS-$^{13}$C weathered for 2400 h. Both spectra are normalised to the same total intensity. Thus, the individual intensities may vary.
Table S3  Values for $T_{\text{IS}}$ and $T_{1\rho}^{1H}$ as determined from the refinements of the build-up curves shown in Fig. 3a. The experimental and fitting error for each value is assumed to be around 10%, but much higher for the ketal resonance due to the low signal to noise ratio. The average $T_{1\rho}^{1H}$ is about $3000 \mu s \pm 900 \mu s$. Peak (a) and (a') and (b) and (b'), respectively, were evaluated together due to the fact that the shoulder is not distinguishable from the main resonance for low and very high contact times. Furthermore, both show a similar $T_{\text{IS}}$ and $T_{1\rho}^{1H}$.

|                | ketones (a) | carboxy groups (b) | ketals (c) | peroxides (d) | alcohols (e) | aromatic ipso C | aromatic CH | aliphatic CH, CH$_2$ |
|----------------|-------------|---------------------|------------|---------------|--------------|----------------|-------------|---------------------|
| $T_{\text{IS}} / \mu s$ | 387         | 1000                | 1700       | 365           | 148          | 480            | 101        | 89                  |
| $T_{1\rho}^{1H} / \mu s$ | 3860        | 2820                | 3500       | 3560          | 3550         | 3050           | 2220       | 1800                |

Table S4  $I_{\infty}$ calculated according to equation 2. $T_{1\rho}^{1H}$ and $T_{\text{IS}}$ were taken from Table S3. $I_{\infty}$ smaller than one shows that the nominal intensity for the individual resonance is not reached for the chosen multiCP conditions. The prediction is made according to the I-S model and does not strictly account for chemical groups with strong heteronuclear dipolar couplings like CH and CH$_2$ units.

| weathering time and multiCP parameters | ketones (a) | carboxy (b) | ketals (c) | peroxides (d) | alcohols (e) | aromatic ipso C | aromatic CH | aliphatic CH, CH$_2$ |
|----------------------------------------|-------------|-------------|------------|---------------|--------------|----------------|-------------|---------------------|
| 0 h, 250μs, 12 blocks, $\tau_{\text{CP}}^{\text{tot}} = 3$ ms | 0.965       | 0.955       | 0.964      | 0.962         | 0.957        | 0.957          | 0.926       | 0.907               |
| 1900 h, 250 μs, 8 blocks, $\tau_{\text{CP}}^{\text{tot}} = 2$ ms | 0.965       | 0.955       | 0.964      | 0.962         | 0.957        | 0.957          | 0.926       | 0.907               |
| 2400 h, 150 μs, 13 blocks, $\tau_{\text{CP}}^{\text{tot}} = 1.95$ ms | 0.980       | 0.973       | 0.979      | 0.978         | 0.976        | 0.975          | 0.959       | 0.949               |
| 2400 h, 150 μs, 20 blocks, $\tau_{\text{CP}}^{\text{tot}} = 1.95$ ms | 0.980       | 0.973       | 0.979      | 0.978         | 0.976        | 0.975          | 0.959       | 0.949               |
| 2400 h, 250 μs, 8 blocks, $\tau_{\text{CP}}^{\text{tot}} = 2$ ms | 0.965       | 0.955       | 0.964      | 0.962         | 0.957        | 0.957          | 0.926       | 0.907               |
| 2400 h, 250 μs, 12 blocks, $\tau_{\text{CP}}^{\text{tot}} = 3$ ms | 0.965       | 0.955       | 0.964      | 0.962         | 0.957        | 0.957          | 0.926       | 0.907               |
| 2400 h, 500 μs, 6 blocks, $\tau_{\text{CP}}^{\text{tot}} = 3$ ms | 0.925       | 0.910       | 0.929      | 0.919         | 0.902        | 0.910          | 0.835       | 0.796               |
| 2400 h, 1000 μs, 3 blocks, $\tau_{\text{CP}}^{\text{tot}} = 3$ ms | 0.837       | 0.818       | 0.858      | 0.823         | 0.787        | 0.808          | 0.668       | 0.604               |
Table S5 Relative intensities of the PS-\(^{13}\)C resonances for the ipso C, the aromatic CH units and the aliphatic CH and \(\text{CH}_2\) groups for different weathering times and multiCP conditions before and after correcting with \(I_\infty\) given in Table S4. All relative intensities are normalized with respect to the intensity of the ipso carbon. An average intensity ratio of 1: 5.4: 22.0 is observed by combining all multiCP experiments with block lengths of 250 ms and 150 ms.

| weathering time and multiCP parameters | ipso C \(/ I_\infty\) | ipso C \(/ I_\infty\) | aromatic C's \(/ I_\infty\) | aromatic C's \(/ I_\infty\) | aliphatic C's \(/ I_\infty\) | aliphatic C's \(/ I_\infty\) |
|----------------------------------------|------------------|------------------|---------------------|---------------------|-------------------|---------------------|
| 0 h, 250 µs, 12 blocks, \(\tau_{\text{CP}} = 3\) ms | 1                | 1                | 5.1                 | 5.3                 | 22.4              | 23.6              |
| 1900 h, 250 µs, 8 blocks, \(\tau_{\text{CP}} = 2\) ms | 1                | 1                | 5.4                 | 5.4                 | 21.8              | 23.1              |
| 2400 h, 150 µs, 20 blocks, \(\tau_{\text{CP}} = 3\) ms | 1                | 1                | 5.5                 | 5.6                 | 22.6              | 23.4              |
| 2400 h, 250 µs, 12 blocks, \(\tau_{\text{CP}} = 3\) ms | 1                | 1                | 5.3                 | 5.3                 | 21.1              | 21.6              |
| 2400 h, 250 µs, 8 blocks, \(\tau_{\text{CP}} = 2\) ms | 1                | 1                | 5.5                 | 5.6                 | 22.3              | 23.5              |
| 2400 h, 500 µs, 6 blocks, \(\tau_{\text{CP}} = 3\) ms | 1                | 1                | 4.3                 | 4.8                 | 16.1              | 19.2              |
| 2400 h, 1000 µs, 3 blocks, \(\tau_{\text{CP}} = 3\) ms | 1                | 1                | 4.0                 | 5.1                 | 14.3              | 20.2              |

Table S6 Correction factors \(c_i\) of the distinct resonances, derived from intensities of the \(^{13}\)C multiCP and CP NMR spectra for the same sample. The multiCP intensities were not corrected with \(I_\infty\) before calculating the \(c_i\) values.

| functional group | PS-\(^{13}\)C multiCP 250 ms 8blocks | PS-\(^{13}\)C multiCP, different parameters, 2400 h |
|------------------|-----------------------------------|--------------------------------------------------|
|                  | \(c_i\) 2400 h | \(c_i\) 1900 h | 1000 µs 3 blocks | 500 µs 6 blocks | 250 µs 12 blocks | 150 µs 20/13 blocks |
| ketones          | 0.73               | 0.73               | 0.99               | 0.93               | 0.76               | 0.74               |
| carboxy groups   | 0.61               | 0.59               | 1.04               | 0.96               | 0.70               | 0.64               |
| peroxides        | 0.73               | 0.67               | 1.01               | 0.95               | 0.76               | 0.67               |
| alcohols         | 0.74               | 0.65               | 0.95               | 0.85               | 0.69               | 0.61               |
| ipso C           | 0.68               | 0.69               | 0.94               | 0.87               | 0.68               | 0.67               |
| arom. C's        | 0.95               | 0.91               | 1.0                | 0.97               | 0.92               | 0.93               |
| aliphatic C's    | 1.06               | 1.07               | 0.99               | 1.02               | 1.06               | 1.07               |
Table S7 Correction factors \( c_i \) of the distinct resonances, derived from intensities of the \(^{13}\)C multiCP and CP NMR spectra for the same sample. The multiCP intensities were corrected with \( I_\infty \) before calculating the \( c_i \) values.

| functional group | PS-\(^{13}\)C multiCP 250 ms 8blocks | PS-\(^{13}\)C multiCP, different parameters, 2400 h |
|------------------|---------------------------------|-----------------------------------|
|                  | \( c_i \), 2400 h | \( c_i \), 1900 h | 1000 μs | 500 μs | 250 μs | 150 μs |
| ketones          | 0.68              | 0.7              | 0.76   | 0.81   | 0.73   | 0.72   |
| carboxy groups   | 0.59              | 0.56             | 0.81   | 0.86   | 0.67   | 0.62   |
| peroxides        | 0.69              | 0.65             | 0.78   | 0.85   | 0.71   | 0.65   |
| alcohols         | 0.71              | 0.63             | 0.76   | 0.76   | 0.65   | 0.59   |
| ipso C           | 0.65              | 0.66             | 0.74   | 0.78   | 0.7    | 0.66   |
| arom. C’s        | 0.94              | 0.9              | 0.95   | 0.94   | 0.97   | 0.93   |
| aliphatic C’s    | 1.07              | 1.08             | 1.05   | 1.04   | 1.06   | 1.07   |

Fig. S10 Comparison of multiCP \(^{13}\)C MAS NMR spectra (red line: \( \tau_{\text{block, multiCP}} = 250 \mu s \) with 12 blocks and \( \tau_{\text{total, CP}} = 3 \) ms; black line: \( \tau_{\text{block, multiCP}} = 500 \mu s \) with 6 blocks and \( \tau_{\text{total, CP}} = 3 \) ms) for commercial unadditivated PS weathered for 3200 h. Both spectra are normalised to the same total intensity. The black boxes mark the cut-outs which are shown in the insets.
S2 Calculations of $^{13}$C enrichment

One would expect an intensity ratio of around 1:5:20 in the labelled sample. The factor 20 results from one aliphatic CH$_2$ Carbon and 20% labelled aliphatic CH carbons (corresponding to ca. 19% enrichment). However, the deconvolution of the multiCP spectra for zero weathering (0 h) (see Table S4) gives an average ratio of 1 : 5.1 : 22.4. The relative intensity (normalized to an intensity of 1 per carbon) of the CH, CH$_2$ resonance at 43 ppm in dependence of the share $c$ of the labelled carbons on the total number of carbons at the $\alpha$-position is given by:

$$1 + (c \cdot 99\% + (1 - c) \cdot 1.1\%) /1.1\% = 22.4. \quad (3)$$

A share $c$ of the CH carbons is labelled and 99% $^{13}$C enriched and a share (1-$c$) of the CH carbons occurs in natural abundance (1.1%). The plus 1 stems from the intensity of the CH$_2$ carbons. This intensity ratio of 22.4 corresponds to a share $c = 22.8\%$ of labelled carbons and approximately 23.4% $^{13}$C enrichment for the aliphatic CH.

S3 Calculation of defect proportions

To calculate the defect proportions, the selective $^{13}$C enrichment of 23.4% at the $\alpha$ position of PS needs to be considered. It is assumed that the generated peroxy, carbonyl, carboxy and hydroxy groups are all situated at the labelled C atom due to the stabilisation of benzyl radicals. Thus, their signal intensity will be overestimated by a factor of 21.3, since:

$$\frac{(0.228 \cdot 99\% + 0.772 \cdot 1.1\%)}{1.1\%} = 21.3 \quad (4)$$

Hence, the defect signal intensities need to be divided by 21.3. For the superimposed aliphatic backbone signals a factor of 11.1 needs to be considered, since:

$$\frac{(1.1 + 0.228 \cdot 99\% + 0.772 \cdot 1.1\%)}{(1.1\% \cdot 2)} = 11.1 \quad (5)$$

Subsequently, the defect proportions were calculated according to Meides et al.\textsuperscript{17} with the following equations:

$$p_{ru} = \frac{1 - (8 \cdot I_{ketone}) - (2 \cdot I_{COOH}) - (8 \cdot I_{POOH}) - (8 \cdot I_{OH})}{8} \quad (6)$$

with:

- $p_{ru}$: proportion of styrene 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.

The ratio of the different functional groups is $I_{ketone} : I_{COOH} : I_{POOH} : I_{OH} : p_{ru}$. Thus, with the knowledge of $p_{ru}$ the absolute proportions of the carbonyl groups (ap$_{ketone}$), carboxy groups (ap$_{COOH}$), peroxy groups (ap$_{POOH}$) and hydroxy groups (ap$_{OH}$) can be calculated:

$$ap_{ketone} = \frac{I_{ketone}}{(p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH})} \quad (7)$$

$$ap_{COOH} = \frac{I_{COOH}}{(p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH})} \quad (8)$$

$$ap_{POOH} = \frac{I_{POOH}}{(p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH})} \quad (9)$$

$$ap_{OH} = \frac{I_{OH}}{(p_{ru} + I_{ketone} + I_{COOH} + I_{POOH} + I_{OH})} \quad (10)$$