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1 **Fate of polystyrene and polyethylene nanoplastics exposed to UV in water**

2

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10 **Abstract**

11

12 The possible presence of plastic particles with a size smaller than 1 μm in the aquatic
13 environment raises widespread concern over their environmental impact. Therefore, it is
14 important to understand whether and to what extent nanoplastics dispersed in water degrade
15 under UV irradiation. To address this issue, we studied the effect of UV irradiation on
16 monodisperse polystyrene (PS) latex particles with hydrodynamic radii 0.10, 0.25, 0.52, and
17 2.5 μm as well as on polydisperse polyethylene (PE) particles with an average hydrodynamic
18 radius of 0.35 μm . The degradation rate of both polymers was studied under high intensity
19 UV irradiation, while only the degradation of PS was studied under simulated sunlight, as the
20 degradation of PE was too slow in this case. The degradation was characterized with light
21 scattering techniques, confocal laser scanning microscopy, UV visible spectroscopy, and total
22 organic carbon (TOC) analysis. All particles were found to fully degrade, but the degradation
23 rate of PS particles was much faster than that of PE particles. Aggregation of PS particles

24 after the addition of sea salt did not inhibit their degradation under UV irradiation. TOC
25 analysis showed that the large majority of the carbon of the polystyrene was converted into
26 volatile products. Interestingly, both polymers, PS and PE, showed no change in the radius of
27 the particles until their mass had decreased by more than 70%, implying that degradation
28 mainly occurred within the particles through the release of organic molecules. The formation
29 of hollow particles and their final fragmentation were confirmed by CLSM microscopy. It
30 was estimated that complete degradation of nanoplastics dispersed in water and exposed to
31 simulated sunlight takes about a month for PS and 2 years for PE, assuming that the effect of
32 the radiation intensity was the same for PE as was determined for PS.

33

34 **KEYWORDS.** Nanoplastics, microplastics, nanoparticles, UV irradiation-induced
35 degradation, polyethylene, polystyrene

36

37 **1. Introduction**

38 There is growing concern over plastic waste in the marine environment. In the last 50
39 years, huge quantities of plastics entered the aquatic environment where they have been
40 accumulating with unknown lifetimes^{1, 2}. Once in the marine environment, plastics undergo
41 transformation, weathering and degradation and with possible fragmentation and/or erosion
42 leading to the formation of microplastics and nanoplastics. Microplastics constitute a huge
43 family of particles with sizes up to 5 mm displaying various shapes and chemical natures
44 making it difficult to characterize their impact on marine life^{3, 4}. Secondary nanoplastics with
45 a size smaller than 1 μm can be released from macro and microplastics by strong mechanical
46 abrasion of plastics such as milling⁵ or rotational abrasion⁶, but may also be the result of
47 weathering^{3, 7, 8, 19, 9-11}. In addition, primary micro- and nanoplastics are used in a range of
48 industrial products and may be unintentionally released into the environment¹². Ter Halle et

49 al ¹³ reported for the first time their presence in the North Atlantic Gyre. Since then,
50 nanoplastics have also become an increasing concern as their impact on organisms might be
51 very important ^{14, 15}.

52 Whereas, the breakdown of macroplastics into micro and nanoplastics under
53 environmentally relevant conditions has been investigated extensively in the last years ^{3, 8,7, 19,}
54 ^{9-11, 16}, relatively few studies have reported on the ultimate fate of nanoplastics in the aquatic
55 environment under UV-irradiation ¹⁷. Concerning microplastics, very recently, Liu et al. ¹⁸
56 reported a study of the degradation of polystyrene (PS) microparticles suspended in water
57 during high intensity UV-irradiation in which they measured the size and number of the
58 resulting particles. They observed that initially cavities were formed within the particles that
59 subsequently break-up into smaller ones ¹⁸ with the production of large amounts of
60 nano/microsize fragments. Zhu et al ¹⁹ studied the degradation of several types of
61 microplastics under sunlight and they showed that dissolved organic carbon (DOC) was the
62 major by-product of sunlight-driven plastic photodegradation. Similarly, Ward et al ²⁰ showed
63 that the complete oxidation of PS particles could occur within decades, producing CO₂ and
64 dissolved organic carbon as the main products. Considering that nanoplastics are smaller than
65 microplastics, it could be expected that their conversion into dissolved organic carbon should
66 be quite fast. However, Paik et al ²¹ reported that the lifetime of thermodegraded
67 polypropylene nanoparticles was moderately high compared to the polypropylene
68 microparticles and other studies suggested that fragmentation process could be limited at
69 small scales ²². Understanding the fate of nanoplastics is very important in view of their
70 persistence and accumulation and their possible release of toxic plastic leachates and
71 degradation products.

72 Therefore, the objective of the present study was to understand the fate of nanoplastics
73 suspended in water under the influence of UV irradiation. Aqueous suspensions of

74 commercial monodisperse PS latex particles with different well-defined sizes and
75 polydisperse PE nanoparticles that were prepared as described elsewhere ²³, were irradiated
76 using a high intensity UV lamp. Complete degradation under simulated sunlight could be
77 studied for PS particles, but was too slow to achieve for PE particles. The molar mass and
78 hydrodynamic radius were measured as a function of the irradiation time using static and
79 dynamic light scattering techniques. As far as we know, this is the first investigation where
80 both static and dynamic light scattering techniques were combined to understand the photo-
81 degradation mechanism of nanoplastics in water. We will show that measuring both the molar
82 mass and the hydrodynamic radius during the degradation process is needed to fully describe
83 the degradation mechanism. Moreover, the total organic carbon in the aqueous phase was
84 monitored and allowed us to show the formation of volatile breakdown products.

85 PS is a major pollutant, but we are aware that understanding the degradation of PE is
86 more relevant as it is far more common in the environment. Nevertheless, in this study PS
87 particles were studied in more detail than PE particles, because they are commercially
88 available in many well-defined sizes and degrade much faster. PS particle suspensions are
89 therefore excellent model systems to study the effect of size on the degradation mechanisms
90 and speed. The comparison of light scattering measurements on PS and PE particles during
91 irradiation showed that the degradation process on the colloidal length scale is similar even
92 though it occurs at different rates. As indicated above, PE degradation was found to be too
93 slow under simulated solar irradiation for the study to be feasible. However, we were able to
94 obtain realistic estimates of the degradation rate of PE nanoparticles in the natural
95 environment by assuming that the effect of high-intensity UV irradiation and simulated solar
96 irradiation on the degradation rate of PS nanoparticles was approximately the same for PE
97 particles. To the best of our knowledge, this is the first study in which both the change of

98 molar mass, size and structure of the small micro- and nanoplastics and the release of volatile
99 organic carbon were monitored during photodegradation.

100

101 2. MATERIALS AND METHODS

102 2.1. Materials

103 Model polystyrene latex particles with 4 different hydrodynamic radii (R_{hz}) varying by
104 more than one order of magnitude ($R_{hz} = 0.10, 0.25, 0.52$ and $2.5 \mu\text{m}$) were purchased from
105 Polysciences. According to the provider, the particles were negatively charged due to the
106 presence of carboxylate groups on their surface which make them stable against aggregation.
107 The $2.5 \mu\text{m}$ particles contain some divinylbenzene as the cross-linker. However, all other
108 particles are free of any additives. The density of the polystyrene particles was 1.05 g/cm^3 .

109 Polyethylene particles were prepared without any surfactant using an emulsions of
110 toluene in water with PE dissolved in the toluene phase as described in reference ²³. The
111 toluene and water were removed by freeze-drying the emulsion which yields PE particles with
112 R_{hz} ranging between 0.2 to $0.8 \mu\text{m}$. After freeze-drying, the PE powder was free of toluene
113 which was confirmed with Raman spectroscopy and thermogravimetric analysis. It was
114 shown that a small amount of PE particles could be dispersed in ultra-pure water without
115 adding a surfactant forming a stable dilute suspension. It was speculated that the stability was
116 in this case due to accumulation of charges onto the particles. The suspension of PE particles
117 was filtered through $1 \mu\text{m}$ pore size filters. Light scattering measurements showed that after
118 filtration, the R_{hz} of the PE particles ranged between 0.1 - $0.5 \mu\text{m}$ with an z-average $R_{hz} = 0.35$
119 μm .

120

121 2.2. Light scattering

122 Static and dynamic light scattering measurements were done using commercial
123 equipment ALV/CGS3 (ALV-Langen, Germany) and quartz cells containing either PS or PE
124 particles in ultrapure water. We verified that at the low concentration (5 mg/L) at which these

125 measurements were done the effect of interaction between the particles was negligible. The
126 light source was a He-Ne laser with wavelength $\lambda = 632$ nm. The temperature was controlled
127 by a thermostat bath at 20 ± 0.2 °C. Measurements were made at angles of observation (θ)
128 between 13 and 150 degrees which correspond to a scattering vector (q) range between 3×10^6
129 and 3×10^7 m⁻¹. We have used toluene as the standard.

130 In a static light scattering experiment, the time-averaged scattering intensity of the
131 sample (suspended particles and solvent) was measured as a function of θ . The relative
132 intensity of the suspended particles, I_{rel} , was then calculated by subtracting the intensity of
133 the solvent and dividing by that of a standard, for which we used toluene. I_{rel} is related to the
134 weight average molar mass (M_w) and the structure factor ($S(q)$)²⁴⁻²⁶ of the particles
135 according to:

$$136 \quad I_{rel} = K C M_w S(q) \quad (1)$$

137 where K is an optical constant that depends on the setup and the specific refractive index
138 increment of the solute. $S(q)$ describes the dependence of the scattered intensity on the
139 scattering vector q and for particles of any shape, the initial q -dependence of $S(q)$ can be
140 expressed as a series expansion in terms of the z -average radius of gyration (R_g).

$$141 \quad S(q) = \left[1 + \frac{q^2 R_g^2}{3} + \dots \right]^{-1} \quad (2)$$

142 In dilute solution, $S(q)$ depends on the shape of the particles and is equal to 1 for $q \rightarrow 0$. In
143 order to measure the molar mass of particles with light scattering the condition $q \cdot R \ll 1$ must
144 be met. This cannot be done for particles with $R = 2.5$ μm where we can detect no plateau
145 values for I_{rel} at the lowest investigated q values by opposition to what is shown in fig. 1 and
146 fig. S6.

147 In a dynamic light scattering experiment, fluctuations in the scattering intensity around the
 148 time-averaged value discussed above are measured to obtain the diffusion coefficient (D) and
 149 the z-average hydrodynamic radius (R_{hz}) of the particles. First, the autocorrelation functions
 150 of the intensity $g_2(t)$ are measured for different values of θ . Then, the autocorrelation
 151 functions of the electric field ($g_1(t)$) are derived from $g_2(t)$ using the Siegert relation²⁴⁻²⁶. In
 152 this work, $g_1(t)$ was fitted with a monomodal relaxation time distribution ($A(\tau)$) according to :

$$153 \quad g_1(t) = \int A(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \quad (3)$$

154 with

$$155 \quad A(\tau) = H\tau^p \exp\left(-\frac{\tau}{\tau_{gex}}\right)^s \quad (4)$$

156 where H is a normalization constant, τ_{gex} is a characteristic relaxation time and p and s are
 157 parameters that characterized the different shape of the distribution. In dilute solutions the
 158 relaxation time is related to the diffusion coefficient of the particles:

$$159 \quad \tau = 1/(Dq^2) \quad (5)$$

160 R_{hz} can be calculated from D using the Stokes-Einstein relation.

$$161 \quad D = \frac{kT}{6\pi\eta R_{hz}} \quad (6)$$

162 where k is the Boltzman constant, T is the absolute temperature and η the viscosity of the
 163 solvent. In this manner $A(\tau)$, the relaxation time distribution obtained at $q \rightarrow 0$ can be
 164 transformed into a distribution of R_{hz} . The z-average hydrodynamic radius (R_{hz}) was
 165 calculated from the average diffusion coefficient obtained at $q \rightarrow 0$.

166 2.3. Confocal laser scanning microscopy (CLSM)

167 Morphological changes of PS particles in suspension were investigated utilizing a Zeiss LSM
168 800 (Oberkochem, Germany). A water immersion objective lens was used (HCxPL APO 63×
169 NA = 1.2) with a theoretical resolution of 0.1 μm in the x–y plane. The PS particles were
170 fluorescently labelled by adding Nile red or Fluorescein isothiocyanate (FITC) that
171 spontaneously adsorbed to the particles. The stock solutions of Nile red and FITC were
172 prepared in ethanol and in water, respectively. The concentration of the fluorophore was 5
173 ppm in the particle suspension. FITC or Nile red was added after the UV irradiation because
174 they bleach during irradiation. Initially, all the Nile red was bound to the PS particles. At
175 longer irradiation times when most of the PS had degraded we observed the formation of
176 dense and bright crystals of Nile red, which, however, could be easily distinguished from the
177 PS particles. At longer UV irradiation time, we also used FITC to confirm the observations
178 obtained with Nile red.

179

180 2.4. UV-visible spectroscopy

181 The UV-visible spectrum of PS particle suspensions at the different ageing times was
182 recorded with a UV–visible spectrometer (Jasco PAC-743). The absorbance (A) was recorded
183 between wavelengths 200-900 nm with a scan speed of 400 nm/minute at a temperature of
184 20°C. The path length of the light through the cell was 1 cm. With this setup, absorbance
185 measurements are reliable up to 4.

186

187 2.5. Total organic carbon analysis (TOC)

188 TOC analysis was performed on PS latex particles with $R_{hz} = 2.5$ and 0.25 μm and the
189 samples ($C = 100$ mg/L) at different irradiation times were diluted by a factor of 4 before
190 performing TOC measurements. The analysis was done, using a Multi N/C 3100 (Analytik
191 Jena) TOC analyzer equipped with an autosampler. The TOC values are measured based on

192 the integration signals of CO₂ by the infrared detector for total carbon (TC) and total
193 inorganic carbon (TIC). The TOC value is calculated as TOC = TC-TIC. The vials used as
194 containers for the TOC analyses were kept in an oven at 500°C for 8h to avoid any trace of
195 organic matter and cooled down before further use. The conditions used in the method were
196 as follows: from 5 to 8 measurements were performed with a coefficient of variation below
197 2%. The sample volume was 200 µL and the rinse volume was 1 mL. The integration time
198 was 300 s and the stirring rate was fixed to 6. For TC measurements, the combustion
199 temperature was set to 750°C. IC measurements were performed in the IC reactor with H₃PO₄
200 10% wt. For TIC, three calibrations were performed between 0.1 and 100.0 mg/L
201 corresponding to a limit of detection based on the lowest calibration curve equal to 33.7 µg/L.
202 For TC, three calibrations were also performed ranging from 1.0 up to 1000.0 mg/L leading to
203 a limit of detection based on the lowest calibration curve of 112.1 µg/L. The average of three
204 values differing by less than 2% was taken. We note that the measured values were always
205 three times bigger than the detection limit and remained within the calibration range.

206

207 2.6. Irradiation

208 Two kinds of set-ups were used to UV irradiate the PE and PS suspensions. In order to
209 simulate sunlight exposure, the samples were placed in a commercial solar exposure simulator
210 (XLS+ chamber, Atlas), which is equipped with a xenon lamp, see figure S1a. Weathering
211 was achieved with a daylight filter following the ISO 4892-2 standard at 40°C and a black
212 standard temperature of 65°C. The irradiation intensity was 60 W/m², which corresponds to a
213 solar radiation exposure of 216 kJ.m².h⁻¹. To accelerate the process further, the suspensions
214 were also irradiated using a high intensity UV lamp. The high intensity UV lamp (HTC 400-
215 241 SUPRATEC HTC/HTT, OSRAM GmbH) was used without any filter and was fixed
216 inside a black box at a distance of 75 cm from the irradiated samples, see figure S1b of the

217 supplementary information. The same lamp has been used earlier for the accelerated
218 weathering of plastics²⁷. The temperature inside the quartz tubes was between 40 and 50°C
219 due to the heat from the UV lamp. The intensity of the lamp near the sample was around 360
220 W/m², i.e. 6 times higher than with the solar chamber. We note that the spectra of the two UV
221 light sources are not the same, see figure S2

222 For the analysis by light scattering techniques, PE or PS particle suspensions at C = 5
223 mg/L in ultrapure water (Millipore) were placed in capped quartz cells with an inner diameter
224 of 8 mm. The tubes were placed at an angle so that the total path length of the light through
225 the sample was 10 mm. These samples were transparent and the intensity of UV light was
226 almost the same over the whole depth. The samples were regularly homogenized during
227 irradiation and before the light scattering measurements by handshaking.

228 For TOC, CLSM, and UV-visible spectroscopy measurements on PS particles with
229 radii of 2.5 µm and 0.25 µm, a quartz beaker containing 80 ml of the PS suspension at C=100
230 mg/L was placed under the high intensity UV lamp, while gently stirring with a magnetic
231 stirrer to avoid sedimentation and ensure uniform UV exposure. 10 ml of the suspension was
232 removed from the beaker at regular time intervals during the UV irradiation for the TOC
233 analysis. During irradiation, the beaker was closed with a quartz cap and the sides of the cap
234 were sealed with Teflon tape to avoid evaporation. These samples were only weakly turbid,
235 which means that the UV-irradiation was on average less intense than for the dilute samples
236 used for light scattering analysis. Therefore, ageing is expected to be somewhat slower.
237 However, this effect became progressively less important as more of the sample was removed
238 so that the path length through the sample decreased from the initial 80 mm. A scheme of the
239 experimental set-up is shown in figure S3.

240 Two different initial concentrations (c=5 mg/L and C=100 mg/L) of PS particles
241 because for light scattering experiments the sample need to be transparent and therefore

242 diluted whereas visually the breakdown is more easily seen at high concentration. It also
243 allowed us to study the effect of concentration in terms of the penetration of the UV light in
244 more turbid samples.

245 The reproducibility of the treatment was tested by irradiating at least two independent
246 samples of the same systems. The results were combined in figs 3 and 5, which showed that
247 the reproducibility is very good.

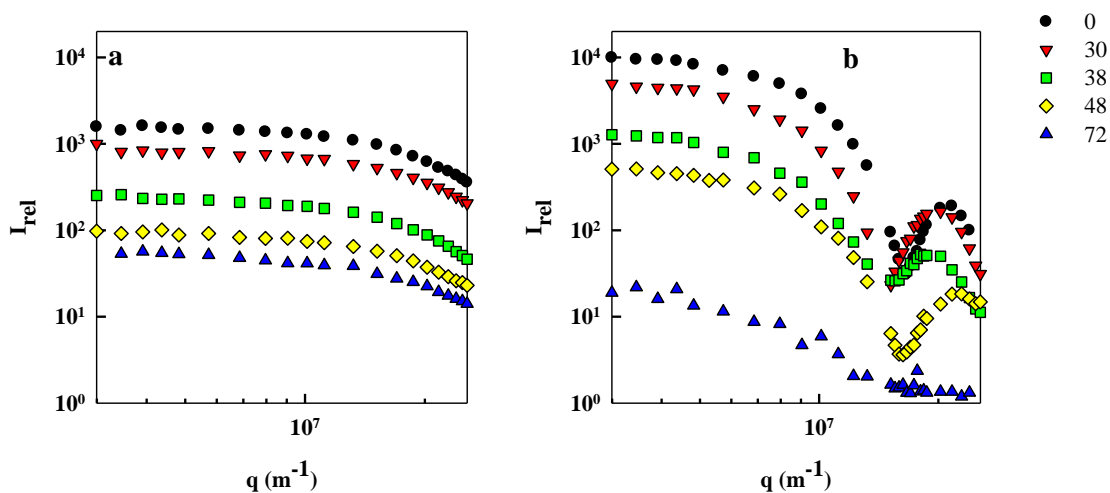
248 **3. Results and Discussion**

249 **3.1. Degradation of PS particles during high intensity UV irradiation**

250 The degradation of the PS particles with initial hydrodynamic radii $R_{hz} = 0.10, 0.25$
251 and $0.52 \mu\text{m}$ was quantified by measuring their molar mass and radius after different UV
252 irradiation times by light scattering techniques. Reliable light scattering measurements require
253 that the suspension is transparent. Therefore, we did these measurements at a low
254 concentration of PS particles ($C = 5 \text{ mg/L}$), at which the suspensions were transparent and
255 interaction between the particles was negligible. This means that all particles received the
256 same irradiation. For comparison, the behaviour of the particle suspensions was also studied
257 as a function of time in the dark. Figure S4 of the supplementary information shows the q -
258 dependence of the scattering intensity for samples kept at different times in the dark. It is
259 characteristic for monodisperse spherical particles and no change was observed even after 120
260 hours indicating that the particles did not degrade when not irradiated. No aggregation upon
261 time was detected either. Note that even weak aggregation is easily detected by light
262 scattering as the scattered light intensity is proportional to the molar mass, see eq. 1.

263 Figure 1 displays the results that have been obtained for the PS particles with $R_{hz} =$
264 $0.10 \mu\text{m}$ and $0.25 \mu\text{m}$ after different UV irradiation times. A systematic decrease of the
265 relative intensity (I_{rel}) was observed with increasing UV irradiation which means that the

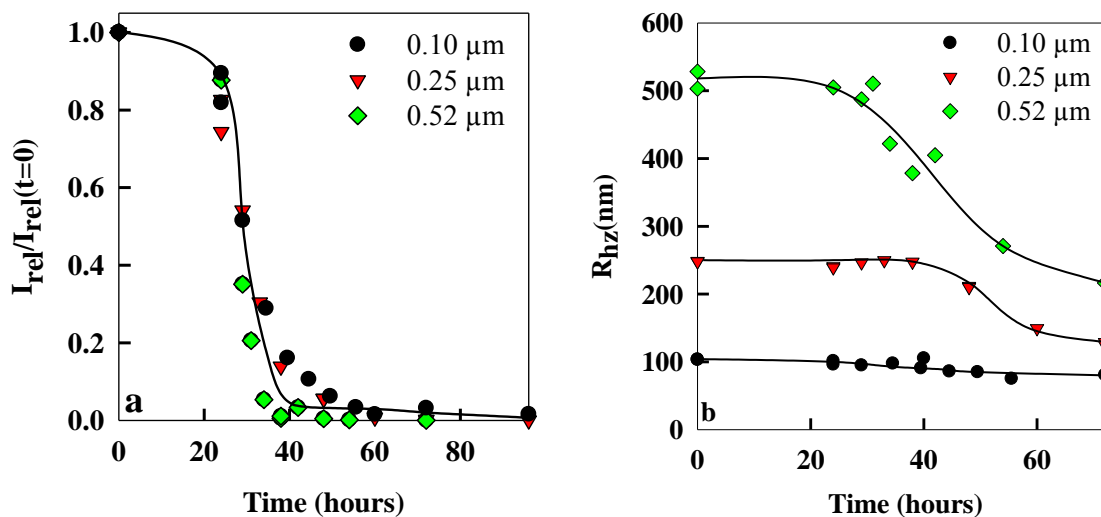
266 molar mass of the particles decreased assuming that their refractive index increment, and thus
 267 K , does not change significantly, see eq. 1. Interestingly, up to 48 h irradiation no significant
 268 change of the q -dependence was observed, which means that the form and size of the particles
 269 remained unchanged. After 72 h irradiation, particles could still be detected. However, the q -
 270 dependence of I_{rel} showed that the particles were no longer spherical and monodisperse. After
 271 96 h, the scattering intensity was not significantly higher than that of Millipore water, see
 272 figure S5 of the supplementary information, and no particles were detected, which shows that
 273 the particles had fully degraded. Similar results were obtained for particles with $R_{\text{hz}} = 0.52$
 274 μm as shown in figure S6 of the supplementary information.



275
 276 Figure 1. Double logarithmic plot of the relative scattering intensity as a function of q for PS
 277 particles in ultrapure water with initial $R_{\text{hz}} = 0.10 \mu\text{m}$ (a) and $0.25 \mu\text{m}$ (b) at different high
 278 intensity UV irradiation times in hours as indicated in the legend which is the same for both
 279 figures.

280 The relative decrease of $I_{\text{rel}}(t)$ at $q \rightarrow 0$ with respect to the initial value is plotted in
 281 Figure 2a as a function of irradiation time showing a sharp decrease after 24 h whatever the
 282 size of the pristine particles. I_{rel} at $q \rightarrow 0$ is proportional to $C \cdot M_w$ if we assume that the specific

283 refractive index increment of the particles does not change significantly upon irradiation, see
 284 eq.1. It seems furthermore reasonable to assume that all particles degrade at approximately the
 285 same rate so that the molar concentration of particles ($v=C/M_w$) does not decrease during
 286 irradiation. It follows that I_{rel} at $q \rightarrow 0$ is proportional to M_w^2 and that the decrease of I_{rel}
 287 implies a decrease in the molar mass of the particles. The relative decrease was the same for
 288 all PS particles, but at longer times ($T \geq 30$ h) the particles with $R_{hz} = 0.52 \mu\text{m}$ degraded more
 289 rapidly. The time needed to decrease by half the amount of PS in the particles can be
 290 estimated from the decrease of the molar mass and was approximately 30 hours for $R_{hz} = 0.52$
 291 μm and 34 hours for the smaller particles. The decrease of the molar mass was observed to
 292 start after some lag-time, which suggests that the removal of material from the particles was
 293 preceded by chemical modifications that need to progress up to a certain point before material
 294 can escape. Notice that figure 2 contains results obtained from independent measurements on
 295 different samples of particles with the same size, showing good reproducibility of the
 296 breakdown process.



297
 298 Figure 2. (a) I_{rel} with respect to the initial value as a function of high intensity UV irradiation
 299 time for suspensions of PS particles at $C=5$ mg/L with three initial radii as indicated in the

300 figure. (b) The average hydrodynamic radius of PS particles with three different initial radii as
301 a function of the irradiation time.

302

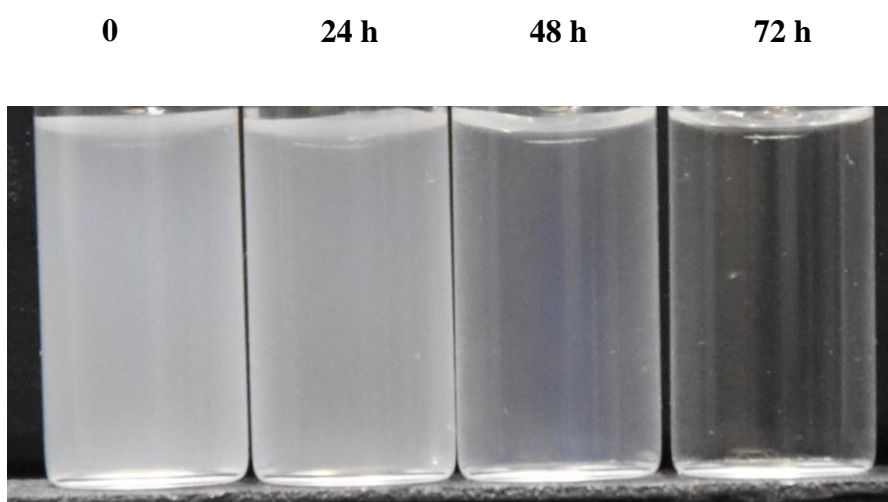
303 Analysis of the autocorrelation functions determined with DLS on the same samples
304 showed narrow relaxation time distributions from which R_{hz} could be determined, as
305 described in section 2.2. The dependence of R_{hz} on the irradiation time is shown in Figure 2b.
306 R_{hz} remained the same up to 40 h for particles with initial $R_{hz} = 0.10$ and $0.25 \mu\text{m}$ and
307 decreased weakly at longer times. The size of particles with initial $R_{hz} = 0.52 \mu\text{m}$ had already
308 decreased significantly after 40 hours of UV irradiation. Interestingly, when comparing fig 2a
309 and b, it appears that the degradation of the particles induced by UV-radiation did not cause a
310 change in their size until their mass had decreased very substantially. The implication is that
311 the material was not preferentially removed from the surface, but rather from the interior of
312 the particles. This degradation phenomenon was induced by UV radiation, as no degradation
313 was observed for particles kept in the dark, see figure S4. UV light can easily penetrate
314 relatively small particles, which explains why degradation occurred everywhere and not
315 specifically on the surface.

316 We also investigated the effect of the initial concentration of PS particles with $R_{hz} =$
317 $0.25 \mu\text{m}$ by increasing the concentration from 5 to 100 mg/L. At $C = 100 \text{ mg/L}$ the suspension
318 was initially turbid, see figure 3. The suspension was irradiated at different UV irradiation
319 times under gentle stirring to avoid uneven exposure to UV. Figure 3 shows the evolution of
320 the visual appearance of a PS particle suspension at different UV irradiation times. The
321 turbidity of the particle suspension decreased with increasing UV irradiation and after 72
322 hours it became transparent. M_w and R_{hz} of the PS particles at different UV irradiation times
323 were determined after dilution to $C = 5 \text{ mg/L}$. In Figure S7(a) we compare the relative

324 decrease of $I_{rel}(t)$ at $q \rightarrow 0$ with respect to the initial value as a function of the irradiation time
325 for particles aged at $C=5$ mg/L and aged at $C=100$ mg/L. The corresponding comparison for
326 R_{hz} is shown in figure S7(b). As expected, the degradation rate was slower for the turbid
327 suspensions due to the lower average irradiation intensity received by the particles. However,
328 in both cases the degradation mechanism was the same, i.e. material was preferentially
329 removed from within the particles.

330

331



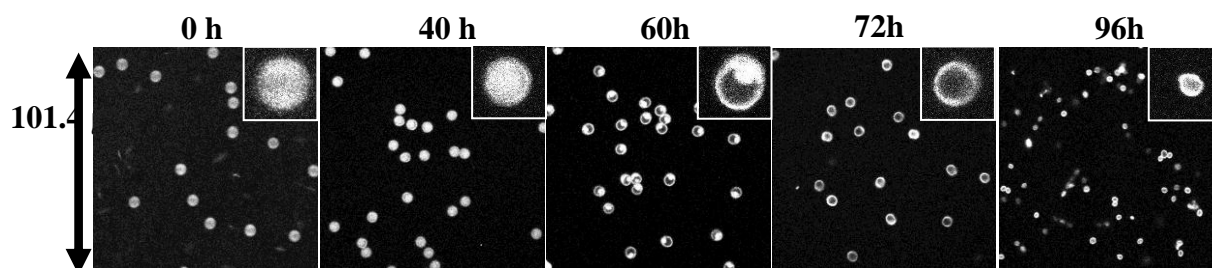
332

333

334 Figure 3. Effect of high intensity UV irradiation time on the turbidity of a suspension of PS
335 particles with $R_{hz} = 0.25$ μm at $C = 100$ mg/L. The particle suspension was stirred gently
336 during irradiation.

337 In order to observe the morphological changes during UV irradiation with CLSM we
338 studied a suspension of larger PS particles with $R_h = 2.5$ μm at $C=100$ mg/L. The particles
339 were stirred gently during irradiation. After the UV irradiation, the particles were labelled
340 with Nile red. We note that no fluorescence was detected without adding a fluorophore.
341 Figure 4 shows images of the PS particle suspensions at different ageing times. Up to 40

342 hours of irradiation the fluorophore rapidly distributed homogeneously throughout the
343 particles. However, after 60 h irradiation, the fluorescence was no longer homogeneously
344 distributed within the particles but appeared to be localized, which suggests the removal of
345 material from the interior of the particles. After 72 h most particles showed a strong
346 fluorescent shell with almost no fluorescence from the inside. After 96 h UV irradiation,
347 smaller particles were formed, probably due to the break-up of larger ones. Finally, no
348 particles were detected after 120 h of UV irradiation. It is clear that all particles were broken
349 down at approximately the same rate, which justifies the assumption that the decrease of the
350 scattering intensity corresponds to a decrease of the molar mass of the particles. These results
351 are in agreement with those reported by Liu et al¹⁸. mentioned in the Introduction.



352
353 Figure 4 CLSM images of a PS particle suspension ($R_{hz} = 2.5 \mu\text{m}$) at high intensity UV
354 irradiation times as indicated in the figure. Images of individual particles at higher
355 magnification ($7.5 \mu\text{m} \times 7.5 \mu\text{m}$) are shown in the insets. The particle suspension at $C = 100$
356 mg/L was stirred gently during irradiation.

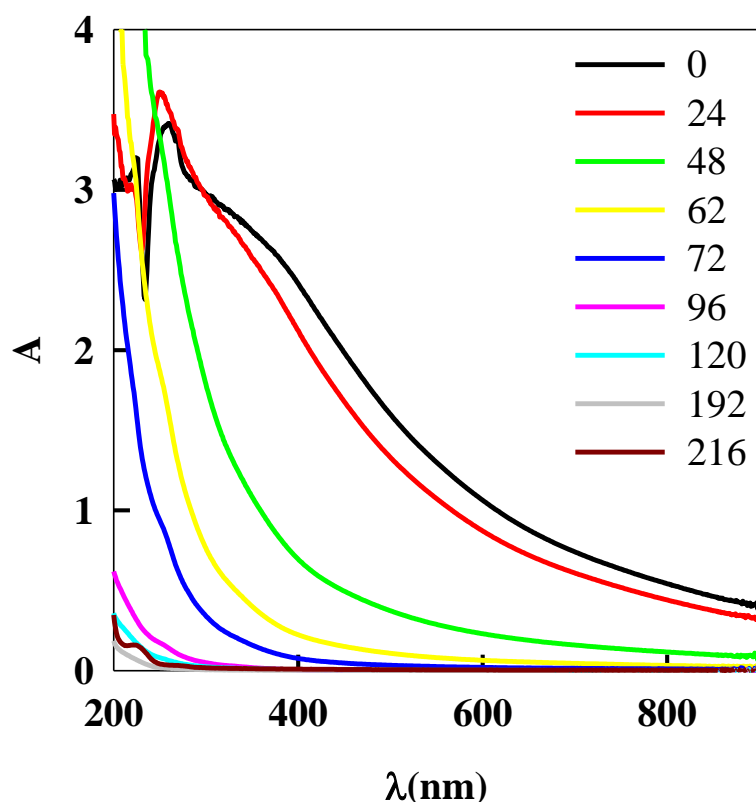
357 The results from light scattering and confocal microscopy are in agreement and show
358 that the degradation of PS particles upon irradiation was not restricted to their surface.
359 Material was mostly removed from the interior of the particles, which explains why the
360 breakdown occurred at approximately the same rate for particles of different sizes, see figure
361 2a. Here we used spherical particles, whereas nanoplastics formed by weathering or abrasion
362 are not expected to be spherical. However, since the material is mostly removed from the

363 interior of the particles, we don't expect the shape to play a major role in the degradation rate
364 as long as the UV-light can penetrate to the core of the particles. However, if the particles are
365 so large that a significant fraction of the UV light cannot penetrate them, the shape of the
366 particles will become an important parameter to take into account.

367 When the particles sediment or cream and form a thick dense layer, the UV light
368 cannot penetrate all particles. This is what happened when PS particles with $R_{hz} = 2.5 \mu\text{m}$ at
369 $C=100 \text{ mg/L}$, were exposed to UV without stirring, leading to the formation of a thick particle
370 layer at the bottom of the quartz beaker due to sedimentation. It explains why we found that
371 the degradation rate of sedimented particles was slower than when sedimentation was avoided
372 by stirring, see figure S8 and figure S9 of the supplementary information for CLSM images of
373 the particles labelled with Nile red and FITC, respectively. We noticed that FITC adsorbed to
374 the particles only after more than 24 h UV irradiation. The reason is most likely that UV
375 irradiation chemically modified the particles. From figure S8 and figure S9 it is clear that
376 without stirring, only a few particles were degraded from the inside at $t = 72 \text{ h}$, but most of
377 the particles were affected between $t = 96$ and 120 h . After 178 h UV irradiation, smaller
378 particles were also formed. No particles were detected by confocal microscopy after 216
379 hours of UV irradiation. This indicates that the degradation rate was slower without stirring,
380 but in both cases, degradation started from the inside.

381 Figure 5 shows the absorbance spectra of PS particles with $R_{hz}=0.25 \mu\text{m}$ at $C= 100$
382 mg/L after different durations of irradiation while stirring gently. The spectra are in
383 agreement with the UV visible spectrum of polystyrene earlier reported in the literature^{20, 28}.
384 Before irradiation, the spectrum showed an absorbance peak at 250 nm together with the
385 effect of turbidity that decreased with increasing wavelengths. The absorbance peak at 250 nm
386 is due to the aromatic ring of the polystyrene as was reported elsewhere^{20, 28}. After 24 h
387 irradiation, the turbidity of the suspension had decreased, but the amplitude of the absorbance

388 at 250 nm showed a weak increase. However, after 48 h irradiation, the absorbance peak at
389 250 nm had completely disappeared and was replaced by a strong increase of the absorbance
390 at lower wavelengths, whereas the effect of the turbidity continued to decrease. At longer
391 times the absorbance at low wavelengths decreased also and after 120 h irradiation, it had
392 become negligible.

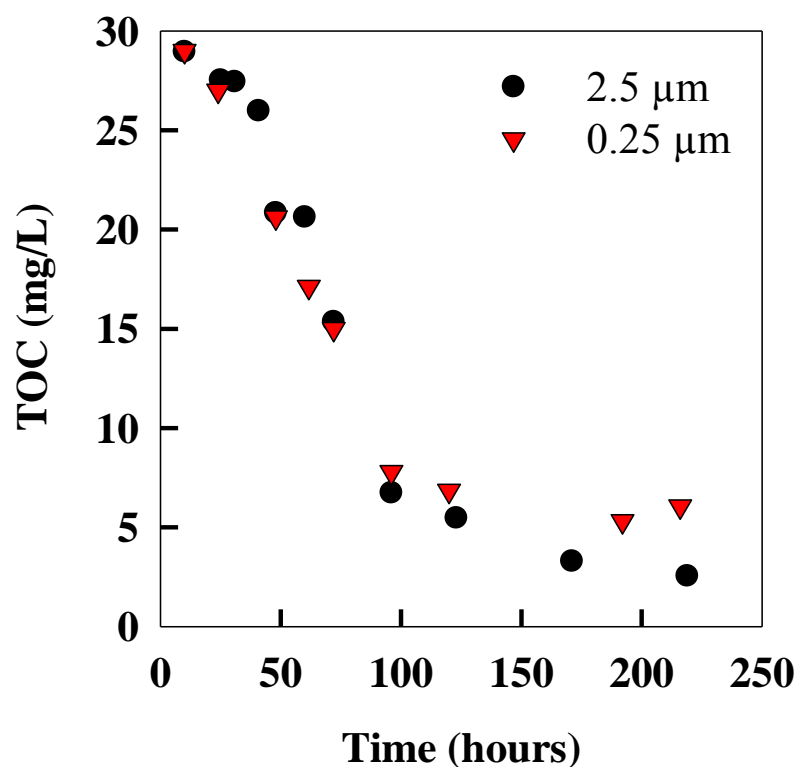


393
394 Figure 5. Absorbance spectra of a suspension of PS particles with $R_{hz} = 0.25 \mu\text{m}$ at 100mg/L
395 as a function of high intensity UV irradiation time as indicated in the graph.

396 The disappearance of the peak at 250 nm suggests that PS was chemically modified
397 within the first 48 h and that breakdown products were formed that strongly absorbed UV
398 light at lower wavelengths. These products were subsequently degraded by further irradiation.
399 Similar results were obtained for PS particles with $R_{hz} = 2.5 \mu\text{m}$ at $C = 100 \text{ mg/L}$ during
400 irradiation while gently stirring, see figure S10 of the supplementary information. Here a

401 strong increase in the absorbance appeared at lower wavelengths that disappeared after longer
402 irradiation times. However, these larger PS particles showed a broad absorbance peak centred
403 at 650 nm of which we do not know the origin. This peak also disappeared during irradiation
404 and after 120 h the absorbance had become negligible.

405 It has been reported that photodegradation of PS leads to the formation of short
406 polymer chains or other small molecules ^{27, 29-32} or even carbon dioxide ²⁰. Here we
407 investigated the total organic carbon content (TOC) of the suspensions of PS particles with R_h
408 = 2.5 and 0.25 μm at different irradiation times, see figure 6. A weak decrease of the TOC
409 was observed until approximately 40 h irradiation followed by a strong decrease. The rate of
410 decrease of the TOC was independent of particle radius up to 120 h of irradiation in
411 agreement with the light scattering results shown above. The decrease shows that PS was
412 broken down into volatile molecules, probably carbon dioxide ²⁰. After 219 h irradiation, the
413 TOC in the solution was reduced from 30 mg/L to 2.5 and 6 mg/L for the particles with R_{hz} =
414 2.5 and 0.25 μm , respectively, see figure 6.

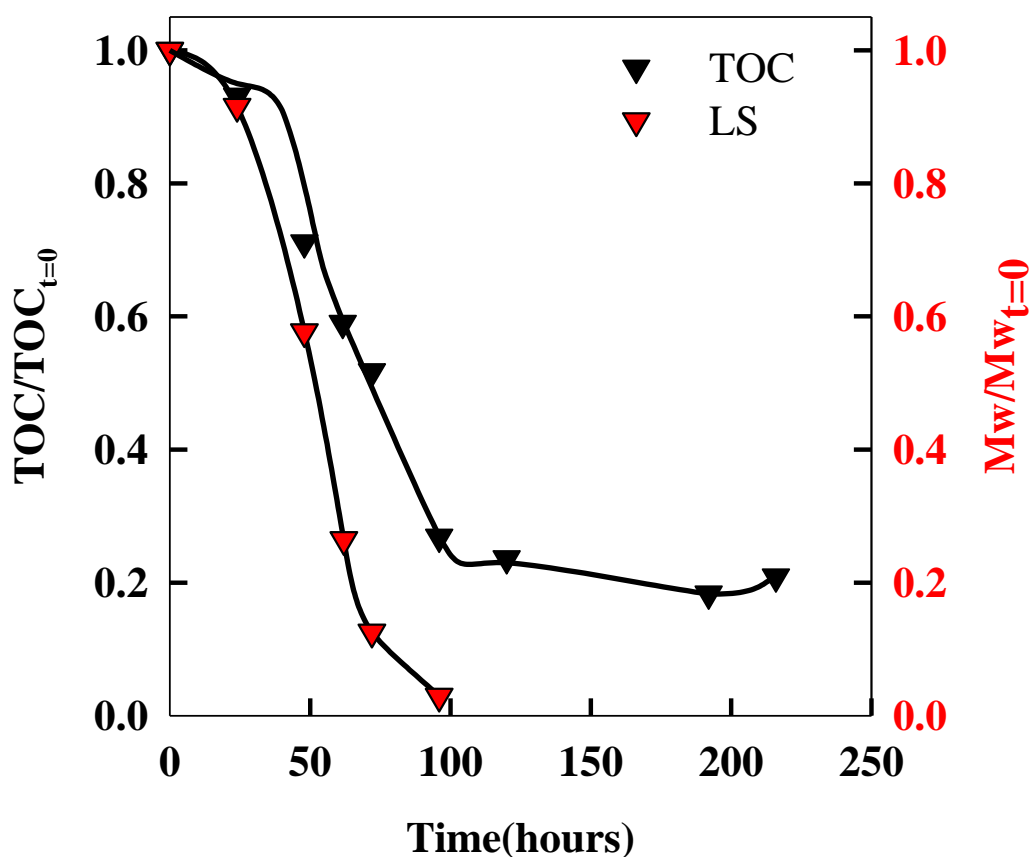


415

416 Figure 6. The decrease of total organic carbon content for a suspension of PS particles with
 417 $R_{hz} = 2.5$ and $0.25 \mu\text{m}$ as a function of high intensity UV irradiation time.

418 At a given UV irradiation time, the TOC consists of both colloidal PS particles and
 419 dissolved carbon formed during degradation. The amount of dissolved carbon can be
 420 estimated for particles with $R_{hz} = 0.25 \mu\text{m}$ by comparing light scattering measurements and
 421 TOC measurements, because the relative decrease of the molar mass of the particles is equal
 422 to the relative increase of the sum of the dissolved and volatilized carbon. In figure 7 the
 423 relative decrease of molar mass was computed from the square root of the relative decrease of
 424 the scattering intensity displayed in figure S7 a. Figure 7 shows that the molar mass decreased
 425 faster than the TOC, which means that the carbon from the PS was first converted into soluble
 426 carbon and subsequently into volatile carbon in agreement with the evolution of the UV

427 spectra. About 20% of the carbon did not volatilize even after very long irradiation times
428 when all the PS particles had long since completely degraded.



429
430 Figure 7. Comparison of the relative decrease of the TOC and M_w with time under
431 high intensity UV irradiation for particles with $R_{hz} = 0.25 \mu\text{m}$, the particle suspension was
432 aged at $C=100 \text{ mg/L}$.

433 As mentioned in the introduction, Ward et al²⁰ showed that photodegradation of PS
434 leads to complete degradation into CO_2 for samples with a thickness below $200 \mu\text{m}$. The
435 authors estimated that in natural sunlight this process takes a few decades assuming that CO_2
436 production increases linearly with UV irradiation times. However, here we observed that in
437 the case of PS the rate of mass loss during UV irradiation is not linear with time but

438 accelerates after some time, see figure 2a. This implies that the time required for the complete
439 degradation of PS in the natural sunlight is much shorter than that estimated by Ward et al ²⁰.

440

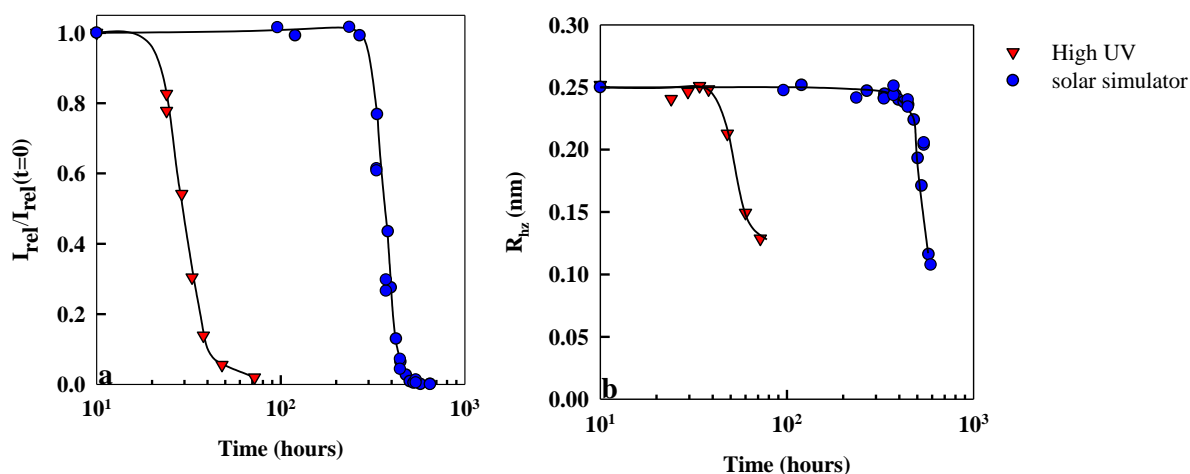
441 **3.2. Degradation of PS particles in simulated sea water**

442 The stability of nanoplastics in the sea may be different from that in salt-free water.
443 Therefore, we studied the degradation of PS particles with $R_{hz} = 0.25 \mu\text{m}$ in simulated
444 seawater produced by adding 35 g/L sea salt to Millipore water, i.e. approximately the same
445 concentration as in natural seawater. Weak aggregation of the particles occurred as soon as
446 the salt was added to the particle suspension, caused by the screening of electrostatic
447 repulsion between the particles by the salt. During the first 24 h of UV irradiation, the
448 aggregates grew in size and became visible to the eye, but subsequently, they disappeared
449 gradually with increasing irradiation time, see figure S11. A transparent solution was formed
450 after 168 h irradiation. UV induced aggregation of nanoplastics in salty water was reported by
451 various authors³³⁻³⁶ but their complete degradation has been rarely discussed in the literature.
452 No significant visual changes were observed in the dark for up to at least 7 days. This
453 observation shows that even if the particles are in the aggregated state, they can be degraded
454 by UV irradiation, albeit at a slower rate.

455 **3.3. Degradation of PS particles during simulated solar irradiation**

456 Figure S12 of the supplementary information shows the evolution of the q-dependent
457 relative scattering intensity of a suspension of PS particles with initial $R_h = 0.25 \mu\text{m}$ after
458 different times of simulated solar irradiation. Three independent measurements were
459 performed for the same particle suspension and a good reproducibility is observed in all cases.
460 The behaviour was similar to that observed during high intensity irradiation, but much slower.
461 In figure 8 the evolution of I_{rel} at $q \rightarrow 0$ and R_{hz} during simulated solar irradiation is compared

462 with that during irradiation with a high intensity UV lamp. The comparison shows that the
 463 breakdown under simulated solar light was about 12 times slower than during irradiation with
 464 a high intensity UV lamp. The difference in degradation rate was larger than the difference in
 465 UV intensity (6 times), which can be explained by the different wavelength distribution of the
 466 two UV sources, see fig. S2 of the supplementary information. Even though the rate is slower
 467 the degradation process appears to be the same with a decrease of the R_{hz} starting only after
 468 I_{rel} had already strongly decreased.

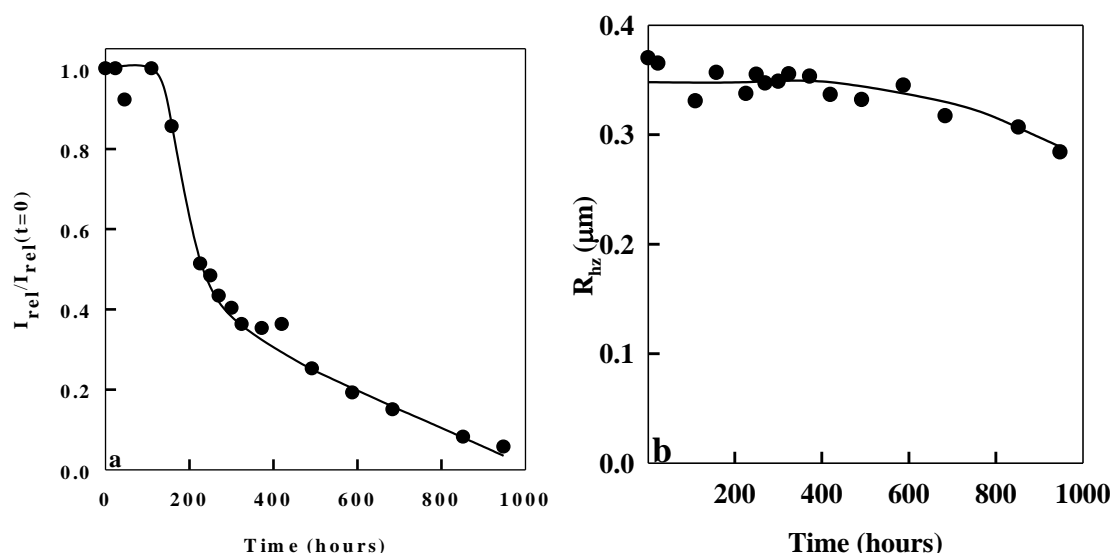


469 Figure 8. (a) The decrease of I_{rel} with respect to the initial value and of (b) the hydrodynamic
 470 radius of PS particles ($R=0.25 \mu\text{m}$) with UV irradiation time. The blue circle and the red
 471 triangle represent data for the aging in the solar simulator and in the high intensity UV lamp,
 472 respectively. The legends are the same in Figure 8a and Figure 8b.

474 3.4. Degradation of PE particles during high intensity UV irradiation

475 The scattering intensity of PE particles at $C = 5 \text{ mg/L}$ in the dark and during
 476 irradiation with the high intensity UV lamp is plotted in Figure S13a and S13b of the
 477 supplementary information, respectively. The suspension of PE particles was observed to be
 478 stable in the dark for at least one month. No creaming was observed despite the density of the

479 PE particles, which can be explained by the low creaming speed given the size of the particles
 480 (approximately 0.003 $\mu\text{m/s}$ for a radius of 0.35 μm and a density of 0.9 g/ml). However,
 481 during irradiation, a systematic decrease in I_{rel} was observed. In figure 9a the dependence of
 482 I_{rel} at $q \rightarrow 0$ on the irradiation time is shown. I_{rel} decreased relatively sharply after about 4 days
 483 of irradiation by about 60% after which the decrease became more gradual. R_{hz} remained
 484 approximately constant for about 25 days after which it decreased weakly, see figure 9b. The
 485 crystalline fraction of the PE used in the investigation was 32%²³. We speculate that the
 486 initial fast decay is due to the degradation of PE in the amorphous region whereas the slow
 487 decay corresponds to the crystalline PE.



488
 489 Figure 9. (a) The decrease of I_{rel} with respect to the initial value (b) and the average
 490 hydrodynamic radius for a suspension of PE particles during high intensity UV irradiation.

491 The degradation rate of PE particles was found to be much slower than that of PS
 492 particles. The time required to reduce 90% of the relative scattering intensity with a high
 493 intensity UV irradiation was around 38 days for PE compared to 2 days for PS particles, see
 494 fig. 9a. Considering that $I_{\text{rel}} \propto M_w^2$, a 90% reduction of the intensity corresponds to a mass

495 loss of 70%. As for PS particles, the time needed to decrease by half the amount of PE in the
496 particles can be estimated from the decrease of the molar mass and was approximately 20
497 days.

498 Interestingly, a similar degradation behaviour was observed for PE as that of PS, i.e.
499 the M_w of the particles was decreased substantially without changing the radius see figure 2
500 and figure 9. However, the degradation rate was much slower for PE, which implies that the
501 chemical reactions leading to the break-down of PE are very different than for PS. However,
502 for both polymers the break-down is caused by UV radiation, which can easily penetrate both
503 the small PS and PE particles studied, which explains why it is much faster using a high
504 intensity lamp than in simulated sunlight. Therefore, it is reasonable to assume that the effect
505 of the UV source on the degradation rate is approximately the same for PS and PE. For PS
506 particles we found that it was 13 times slower under sunlight than under the high intensity UV
507 lamp. Assuming that the degradation rate of PE particles is also 13 times slower under
508 simulated sunlight we find that it will take more than a year to decrease by 70% the molar
509 mass of PE particles suspended in water under simulated solar irradiation.

510 The stronger resistance to UV irradiation of PE compared to PS was also noted in a
511 study by Zhu et al ¹⁹. These authors investigated the photochemical dissolution of buoyant
512 microplastics of PE, PP and expanded PS by monitoring the formation of dissolved organic
513 content (DOC) under natural sunlight exposure. The authors reported that the highest DOC
514 production was for PS followed by PP and then PE. The faster degradation rate of PS is
515 related to its chemical structure which renders it more prone to photo oxidation than
516 polyolefins. Another difference between the PS and PE particles is that the latter was not
517 necessarily spherical. However, given that the degradation rate is independent of the particle
518 size for small particles and starts from the inside, the shape is unlikely to have an influence on
519 the degradation rate except perhaps in the final stage where the particles break-up.

520 The results reported in the current study show that nanoplastics in aqueous suspension
521 degrade more or less slowly under solar radiation depending on their chemical nature.
522 Degradation does not occur in the dark and therefore requires that the particles are near the
523 surface where the intensity of UV irradiation is still significant. If the particles are larger or
524 aggregate into larger flocs they will sink or float depending on their density. Only when they
525 float they will be subjected to irradiation leading to their degradation. In that case, their rate of
526 degradation is expected to be similar to that found here for small particles as long as the UV
527 light can penetrate them, as was shown here for aggregated PS particles. For instance, at least
528 50% of UV light penetrates pure PS to a depth of 100 μm ³⁸. Notice, however, that here we
529 studied pristine PS and PE particles, but in practice, additives that protect against UV or
530 oxygenation can be present. Their presence may lead to a slow-down of the degradation
531 process.

532

533 **4. Conclusion**

534 Nanoplastics made from polystyrene ($R_{\text{hz}} = 0.1 - 2.5 \mu\text{m}$) and polyethylene ($R_{\text{hz}} = 0.1$
535 $- 0.5 \mu\text{m}$) in aqueous suspension fully degrade during irradiation with UV light. Light
536 scattering and CLSM measurements show that initially, mass loss occurs from the interior of
537 the particles rendering the particles increasingly less dense without changing their size.
538 Fragmentation occurs only after the large majority of the mass is lost and the particles have
539 become fragile. The degradation rate was found to be similar for PS particles with radii up to
540 at least 2.5 μm . TOC analysis showed that degradation of PS particles leads to the removal of
541 carbon from the suspension in the form of volatile carbon. The degradation process of PE
542 particles induced by UV irradiation was similar to that of PS particles, but approximately 20

543 times slower than for PS particles. Under simulated sunlight irradiation it takes about one
544 month for PS and 2 years for PE to fully degrade.

545 In more realistic situations it is likely that nanoplastics aggregate. Here we showed for
546 PS particles that the degradation occurs also in the aggregated state. Of course, it is necessary
547 that UV light can penetrate the aggregates, which is easier when they are small and have an
548 open structure. Other issues that will need to be considered in future research are the effect of
549 additives and contaminants that may influence the degradation rate.

550 **Conflicts of interest**

551 There are no conflicts of interest to declare

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555

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