Title: Facile nanoplastics formation from macro and microplastics in aqueous media

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Abstract

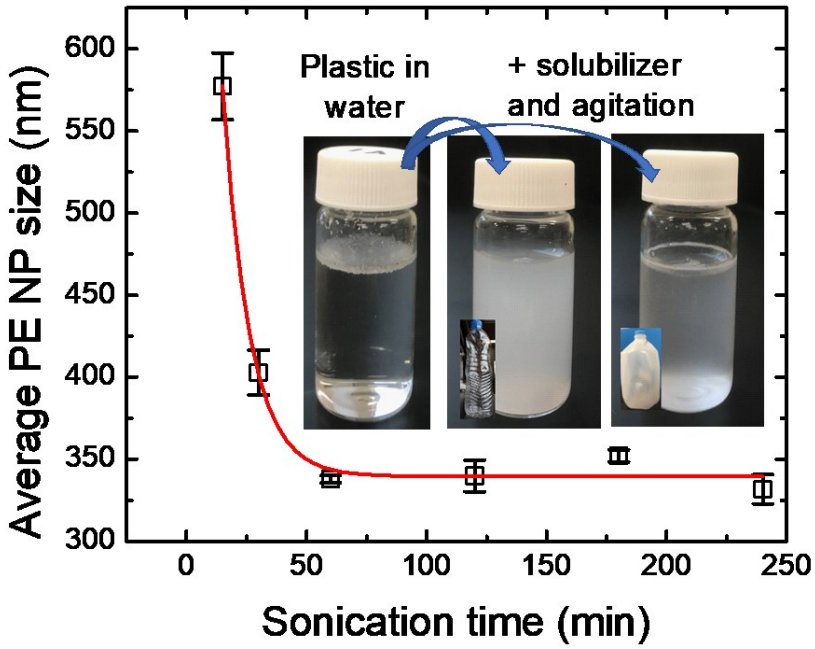
The immense production of plastic polymers combined with their discordancy with nature has led to vast plastic waste contamination across the geosphere, from the oceans to freshwater reservoirs, wetlands, remote snowpacks, sediments, air and multiple other environments. These environmental pollutants include microplastics (MP), typically defined as small and fragmented plastics less than 5 mm in size, and nanoplastics (NP), particles smaller than a micrometer. The formation of micro and nanoplastics in aqueous media to date has been largely attributed to fragmentation of plastics by natural (i.e., abrasion, photolysis, biotic) or industrial processes. We present a novel method to create small microplastics ($\lesssim$ 5 µm) and nanoplastics in water from a wide variety of plastic materials using a small volume of a solubilizer liquid, such as *n*-dodecane, in combination with vigorous mixing. When the suspensions or solutions are subjected to ultrasonic mixing, the particle sizes decrease. Small micro- and nanoparticles were made from commercial, real world and waste (aged) polyethylene, polystyrene, polycarbonate and polyethylene terephthalate, in addition to other plastic materials and were analyzed using dark field microscopy, Raman spectroscopy and particle size measurements. The presented method provides a new and simple way to create specific size distributions of micro- and nanoparticles, which will enable expanded research on these plastic particles in water, especially those made from real world and aged plastics. The ease of NP and small MP formation upon initial mixing simulates real world environments, thereby providing further insight into the behavior of plastics in natural settings.

Keywords: polyethylene, polymeric nanoparticles, particle size, water contaminants, solubilizer, plastics

Highlights:

- Many plastic materials are readily water solubilized as micro and nanoplastics.
- The solubilization of plastics creates suspended particles of different sizes.
- Smaller nanoplastics (NP) can be prepared using ultrasound mixing.
- Aqueous NP solutions are stable in the presence of other dissolved solutes.
- Solubilized real-world NP have different shapes and sizes than commercial NP.

Graphical abstract:



1. Introduction

The ubiquitous presence of microplastics (MP) in the environment is well established, and the increasing number of reports on nanoplastics (NP) suggests a similar, or even greater, extent of their existence and impacts.(Alimi, Budarz et al. 2018, Akdogan and Guven 2019, Peller, Nelson et al. 2020,

Wang, Saade et al. 2021, Yin, Wang et al. 2021, Kutralam-Muniasamy, Perez-Guevara et al. 2022, Martin, Gan et al. 2022, Zhao, Wei et al. 2022, Zhou, Cai et al. 2022) The ongoing rise in manufacture and use of plastic products, notably pandemic-associated materials,(Kutralam-Muniasamy, Perez-Guevara et al. 2022) continuously adds to the increasing environmental and public health exposures to MP and NP. Since the quantification and analyses of NP in real world aqueous environments are much more challenging than MP,(Schwaferts, Niessner et al. 2019, Cai, Chen et al. 2021, Cai, Xu et al. 2021) far less is known about the extent of their existence and their effects on the environment and biological systems.(Lehner, Weder et al. 2019, Cai, Xu et al. 2021, Goncalves and Bebianno 2021) A lesser number of published studies have described the detection of environmental NP, which now include NP released from single use consumer plastics(Zangmeister, Radney et al. 2022) and weathered disposable face masks.(Materic, Kasper-Giebl et al. 2020, Cai, Xu et al. 2021, Morgana, Casentini et al. 2021, Xu, Ou et al. 2022)

Studies suggest that humans are exposed daily to an estimated 74,000-121,000 MP, (Cox, Covernton et al. 2019) or a weekly load of 0.1-5.0 g,(Senathirajah, Attwood et al. 2021) predominantly through ingestion and inhalation. In a tap water study that separated NP using 20, 100, and 200 nm pore filters, a range of 1.67-2.08 μg/L of NP was determined, and most were 58-255 nm in size.(Li, Wang et al. 2022) While NP have recently been detected in drinking water and single use beverage containers that mostly consist of the plastics used in beverage and food containers, i.e., polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), and nylon, the daily exposure is unknown.(Mortensen, Fennell et al. 2021, Zangmeister, Radney et al. 2022)

The sizes and shapes of MP and NP in the environment influence their uptake, adsorption and impacts on living organisms and other substrates.(Ivleva 2021) While larger plastic particles invoke physical effects, such as digestive system blockages,(Yin, Wang et al. 2021) NP and smaller MP can cross biological membrane barriers and disrupt a number of biochemical pathways.(Brown, Wilson et al. 2001,

Wright and Kelly 2017, Holloczki and Gehrke 2020, Lu, Li et al. 2022) Studies of effects of NP on human health indicate a range of disruptive biological processes.(Shen, Zhang et al. 2019) From experiments using human cell lines, researchers reported an increase in reactive oxygen species (ROS) and inflammation upon exposure to PS NP.(Walczak, Kramer et al. 2015, Schirinzi, Perez-Pomeda et al. 2017, Hesler, Aengenheister et al. 2019) When leukocytes isolated from human blood were exposed to functionalized PS NP as small as 20 nm, cytotoxic responses were observed.(Prietl, Meindl et al. 2014) PS NP were also shown to co-transport with lysosomes to a greater degree than other cell organelles in lung tissue.(Deville, Penjweini et al. 2015) Further, gut tissue exposure to NP and MP was found to elicit inflammation,(Fournier, Etienne-Mesmin et al. 2021) and other studies suggest the possibility that NP and MP function as obesogens.(Kannan and Vimalkumar 2021) In addition, chemicals additives in plastic materials are capable of leaching under a number of conditions,(Campanale, Massarelli et al. 2020, Eales, Bethel et al. 2022) and in combination with other chemical contaminants the impacts of NP may be exacerbated.(Almeida, Martins et al. 2019) It is important to note that most laboratory studies of nanoplastics properties and interactions are based on commercial functionalized particles (e.g. polystyrene (PS) microspheres), which may not accurately mimic these real world NP exposures.(Martin, Gan et al. 2022, Zhou, Cai et al. 2022) The study of real world micro- and nanoplastics is one of the many challenges in understanding the extent of exposures and their interactions and effects.(Lai, Liu et al. 2022)

A prevailing view of plastic materials is that their chemical makeup precludes their facile dispersion in aqueous media. While recent studies have provided evidence of plastic particle releases, plastic materials are used in numerous applications (e.g. food containers, medical equipment) based on their hydrophobic properties.(Ahmad, van den Boogaert et al. 2018) Meanwhile, studies have established that mechanical fragmentation, the continual breakage of plastic pieces, or particle embrittlement, occurs as a result of aging or weathering of plastics.(Luo, Zhao et al. 2020, Menzel,

Meides et al. 2022) This is a widely accepted mechanism for MP and NP formation in aqueous media.(Caldwell, Taladriz-Blanco et al. 2022) Very small MP (~ < 10 μm) and NP can disperse homogeneously in water, manifesting colloidal properties, and exhibiting enhanced chemical reactivity and adsorption due to their much greater surface area than larger plastic pieces.(Gigault, ter Halle et al. 2018, Reynaud, Aynard et al. 2022) While the fates of NP in natural aqueous media are still under investigation, a couple of important pathways have been identified: *(i)* encapsulation by biomolecules, described as eco-corona formation or a diverse bio-molecular coating,(Nasser and Lynch 2016, Junaid and Wang 2021) and *(ii)* agglomeration, which has been shown in natural, aqueous environments where organic matter (NOM) and inorganic ions are present.(Cai, Hu et al. 2018, Oriekhova and Stoll 2018, Sun, Jiao et al. 2021, Zhang, Wang et al. 2022)

In general, it is challenging to systematically prepare, isolate, detect and study NP in aqueous media. There is a need for more standardized, real world plastic particles of different sizes, shapes and polymers in aqueous media, to better simulate the effects of micro and nanoplastics in the environment. Manufactured polystyrene nanoplastics particles have been the most utilized for studies on biological systems, but there are concerns that they do not accurately mimic the structures and complexities of real world NP in water and often contain additional chemicals.(Lehner, Weder et al. 2019, Pikuda, Xu et al. 2019) Recently, specific types of NP have been formulated using a variety of methods in efforts to make NP standards for systematic studies. A soap-free emulsion polymerization of styrene and acrylic acid was used to create the corresponding NP in the size range of 350 to 490 nm.(Pessoni, Veclin et al. 2019) The emulsification of PE dissolved in toluene using surfactants produced NP of sizes 200 to 800 nm.(Balakrishnan, Deniel et al. 2019) Laser ablation of PET created variable shapes of NP with an average size of 100 nm.(Magri, Sanchez-Moreno et al. 2018) Fragments of oxidized PS, PET and polylactic acid (PLA) of 100 nm – 1 mm were prepared using strongly basic conditions coupled with 15 hours of ultrasound treatment.(von der Esch, Lanzinger et al. 2020)

The study presented here demonstrates a novel procedure for the rapid formation of small MP ($\lesssim$ 5 μm) and NP in water from a variety of commercial and real-world macro and microplastics. The simplicity of this formation mechanism suggests that small MP and NP (from here on referred to as **sM&NP**) form by this process in natural aqueous environments. A number of sM&NP created by this method have been studied here using microscopy, spectroscopy and particle size analysis to evaluate their size, shape and chemical composition and to begin to elucidate the mechanism for their formation. This new procedure for the standardized formation of NP and small MP may provide a valuable method to create and study real world sM&NP and offer insight into the presence of these plastic particles in natural aqueous systems.

2.0 Experimental

2.1 Chemicals and real-world plastic materials: PE microplastics that are specifically labeled medium density polyethylene (MDPE) were purchased from MilliporeSigma (Burlington, MA, USA) with an average molecular weight (Av Mw) ~ 4,000 g mol^{-1} and an average Mn ~1700, as determined by gel permeation chromatography (GPC), with a density (ρ) of 0.92 g/mL at 25 °C. Ultrahigh molecular weight polyethylene, UHMWPE, average Mw of 3-6 x 10^6. PS, with an Av Mw of 35,000 g mol^{-1} and ρ = 1.06 g/mL at 25 °C, and PP, Av Mw = 12,000 g mol^{-1} and ρ = 0.9 g/mL were also purchased from MilliporeSigma. PET semi-crystalline granules were purchased from GoodFellow (125 Hookstown Grade Road, Coraopolis, PA 15108-9302, USA). Solubilizer compounds *n*-dodecane (>99.0%), 2-dodecanone (>97%), toluene (reagent grade) and kerosene (reagent grade) were sourced from MilliporeSigma. The source of *n*-undecane (synthesis grade) was EMD Millipore Corp. Laboratory water mixtures were prepared with Millipore MilliQ deionized water (18.2 MΩ).

Real world waste plastic materials (milk jug, water bottle, cup and safety glasses) and aged plastics that were collected from the environment were cleaned and thoroughly rinsed with laboratory deionize

142 water and dried prior to use. The identity of these plastic materials was verified using IR Spectroscopy.
143 These plastic materials were either ground into MP sizes using an industrial blender or cut into pieces to
144 represent macro-size plastic.

145 2.2 Formation of NP in water: To 10 mL of deionized water in a 20 mL scintillation vial, 3-10 mg of plastic
146 granules, particles or pieces were added, the vial capped, and the mixture shaken vigorously either by
147 hand or using a vortex mixer. The plastic pieces either floated at the top or settled at the bottom of the
148 vial, according to their density. A syringe was then used to transfer 10-30 µL of *n*-dodecane to the
149 mixture. Controls contained either water and *n*-dodecane or water and the plastic. Each vial was again
150 capped and shaken vigorously for 30-120 seconds, or longer for specific experiments, which resulted in a
151 cloudy suspension of mostly small MP ($\lesssim$ 5 µm). Many of these suspensions were then subjected to
152 ultrasound mixing (40 kHz), typically for 30 minutes or longer. This same procedure was used for the
153 multiple types and sizes of plastic materials and different organic solubilizer compounds. At much higher
154 solubilizer to plastic ratios (e.g. using 500 uL dodecane in 500 mL aqueous solution containing 20 mg
155 plastic), complete dissolution/suspension of the plastic was achieved, allowing quantitative comparisons
156 to be made for the different NP solutions. The removal of the solubilizer in sM&NP aqueous suspensions
157 was done using organic solvent extractions and/or heat treatment. For a 200 mL suspension volume of
158 PE, the extraction was performed using three volumes of 20 mL of toluene, which removed only the
159 solubilizer. Subsequently, residual solubilizer and toluene were removed by heating of the suspension
160 on a hot plate set in the range of 45-85^{o}C. The reduction or removal of the solubilizer was determined
161 using headspace SPME and GCMS, described in our earlier work.(Peller, Mezyk et al. 2021)

162 2.3 Microscope Imaging and Raman Spectroscopy: A Renishaw inVia Qontor confocal Raman
163 microscope, equipped with a Leica DM2700 optical microscope with brightfield and darkfield
164 microscopy capabilities, was used to analyze the formed sM&NP. Droplets of these suspensions were
165 deposited onto stainless-steel slides and dried at 40°C for 1 hr. High spatial resolution Raman spectra

were collected at a rate of 30 seconds/point using a 150X microscope objective from the samples using a 532 nm laser to excite the sample. A 1200 l/mm grating was used, capturing a spectral window from 660 to 3148 cm^{-1}. Prior to data collection, the instrument was calibrated using an internal silicon (Si) sample, setting the first order silicon band to 520.5 cm^{-1}. All post processing, including baseline subtraction using an intelligent polynomial, was performed using the Renishaw WiRE software.

2.4 Particle Size Analysis: Particle size distributions and averages were measured using a Malvern Zetasizer Nano zs90 dynamic light scattering analyzer at room temperature. Nanoparticle solutions (2.0 mL) were transferred to Suprasil UV cuvettes using glass Pasteur pipettes and run in triplicate. Average particle sizes were as calculated using the in-built software analyses.

3.0 Results and Discussion

3.1 Formation of small microplastic and nanoplastic suspensions in water

Recently, it was reported that the radiation-accelerated weathering of PE MP in aqueous media containing low dissolved oxygen led to the formation of *n*-dodecane, which was a scission product adsorbed to the PE.(Peller, Mezyk et al. 2021) Subsequently, it was observed that the addition of small volumes of *n*-dodecane (10-30 µL) to 10 mL aqueous mixtures of PE MP created cloudy suspensions after vigorous shaking. The sM&NP homogeneously dispersed in water were reproducibly made using 18 mL of water, 20 µL of *n*-dodecane and commercial PE microplastic particles. The average size of suspended PE particles in the cloudy suspension, measured after 2 minutes of vigorous hand-shaking, was 1.3 (±0.2) µm. The particle sizes ranged from 600 nm to 2.0 µm for the commercial PE, smaller than the average size of 3.1 ± 0.9 µm and range of 1.8-4.9 µm for (real world) milk jug PE. No particles were detected for mixtures containing only PE in water. Table 1 shows the average particle sizes of the sM&NP that formed suspensions in water after the addition of *n*-dodecane or, in the case of PET, 2-dodecanone. This transition from insoluble macro or microplastics in water to suspended sM&NP was

189 accomplished using pristine, commercial polymers, real-world plastics and aged plastic materials. The
190 solubilizer compound remained in solution for all the measured suspensions. For all three types of
191 plastics, the real-world sM&NP were similar in size to the commercial plastic materials or slightly larger.

192 There are a number of aqueous environments containing plastic materials and forceful mixing of
193 water where organic compounds similar to *n*-dodecane and 2-dodecanone are commonly present. For
194 example, the ubiquitous plastic waste present in marine and fresh waters(Giacomo Avio, Gorbi et al.
195 2017) encounter leaked or spilled oil and fuel in open and coastal areas, as these events have become
196 more frequent.(Dalton and Jin 2010, Peller, Nelson et al. 2020) The guts of aquatic organisms constitute
197 another natural aqueous system with organic molecules that can function as solubilizers when plastic
198 materials (micro or macro) and water encounter loci of energetic mixing.(Benson, Agboola et al. 2022)
199 Foods and drinks in plastic containers that require vigorous shaking, including baby formula in plastic
200 bottles, often provide the necessary conditions for creation of SM&NP.(Li, Shi et al. 2020) Human
201 digestive systems may also be capable of converting the microplastics that are ingested or inhaled to
202 SM&NP by this mechanism.(Lu, Luo et al. 2019)

203 Further processing of these sMP&NP suspensions using an ultrasound bath led to an increase in
204 the solution cloudiness. **Figure 1A** shows a typical mixture of commercial PE MP in water (control), and
205 **Figure 1B** is an example of the sMP&NP suspension created after the addition of *n*-dodecane to the
206 same mixture after one minute of vigorous hand shaking and 30 minutes of ultrasound mixing. This PE
207 suspension was analyzed using Raman spectroscopy and the micro and nanoparticles were verified as
208 PE. The extension of this methodology to other plastics and organic solubilizers, including kerosene,
209 which is a common mixture of hydrocarbons, resulted in similar suspensions and the formation of the
210 corresponding sMP&NP. For example, **Figure 1C** shows a suspension created from a PE milk jug with *n*-
211 dodecane as the solubilizer, and **Figure 1D** is a suspension of polycarbonate (PC) micro and nanoplastics
212 created from 10 mg shavings from a pair of safety glasses with 2-dodecanone as the solubilizer. The

suspension shown in **Figure 1E** was prepared using a 10 mg piece of PET from a water bottle and 20 µL of kerosene as the solubilizer. Controls that contained only water and solubilizer were shaken vigorously, and these temporary mixtures quickly reverted into separate layers. The range of plastics that created suspended particles in water indicates that using this type of solubilizer and shaking is a general methodology for sMP&NP creation in water.

3.2 Ultrasound mixing effects on suspension concentrations and particle sizes

We found that the extent of NP formation, as well as the NP size distribution, is strongly dependent upon the solution sonication time. The concentration of sMP&NP in water is dependent upon the polymer type and the solubilizer compound. Figure 1 demonstrates the range of solution cloudiness that results from this method of sMP&NP formation, indicating the different concentrations and particle sizes that can be selectively altered through condition modifications, such as ultrasound mixing time. PE suspensions up to 0.4 mg sMP&NP/10 mL water can be created using 20 µL of *n*-dodecane and 60 minutes of ultrasound mixing.

In addition, varying the duration of ultrasound mixing provides different particle size distributions, as shown in **Figure 2A** for the commercial plastics medium density polyethylene (MDPE), polystyrene (PS), and ultrahigh molecular weight PE (UHMWPE). The commercial samples were initially mm-sized particles that floated on the water. The time zero size averages shown in **Figure 2A** were generated after the addition of solubilizer and 1.0 minute of vigorous hand-mixing. The average particle size was then found to *decrease* significantly with sonication. For longer sonication times an average minimum value of ca. 340 nm was reached after 60 minutes of sonication for all three NP. After two hours of solution sonication, the particle size distribution slightly broadened (see **Figure 2B**). In addition, for PS and UHMWPE, the average particle size also slightly *increased* with further sonication time.

The sMP&NP from a number of real world (product) plastics created by this method with ultrasound mixing were analyzed and compared to the commercial pure plastics (see also Table S1). The size distributions obtained for commercial MDPE/*n*-dodecane compared to milk-jug PE/kerosene are shown in **Table 2**. The real-world PE shows a slightly larger average particle size for equivalent sonication time, which correlates to the slightly larger particle sizes of these materials after hand-shaking (**Table 1**). Sonicated PET and PS NP had mostly larger peak distribution values than all forms of PE NP, similar to the hand shaking trends. Moreover, these NP suspensions are extremely stable; effectively equal particle size distributions were measured for up to three months after formation (see **Figure 3**). The size distributions of these NP suggest that these polymers are naturally present at an expansive range of sizes in aqueous media. This is important, as studies have shown size-dependent cellular responses to nanoparticle pollutants(Jiang, Kim et al. 2008) and differences in biochemical disruptions for NP of 50 or 100 nm sizes compared to those 200 nm and larger.(Lu, Li et al. 2022, Stock, Bohmert et al. 2022) Therefore, it is essential that NP exposure studies evaluate the effects of a wide range of sizes such as generated in this study.

3.3 Characterization of sMP&NP using optical microscopy and Raman spectroscopy

To confirm the chemical surface identity and analyze shapes of sMP&NP created by this methodology, the formed suspensions were investigated using optical microscopy with Raman spectroscopy. Polyethylene sMP&NP prepared using commercially obtained medium density PE (MDPE) were found to be mostly spherical in shape and ranged in size from a few microns to less than 300 nm in diameter (**Figure 4A**). The acquired Raman spectrum verified the imaged spheres were PE NP (**Figure 5A**) and, in some cases, the measured spectra matched *n*-dodecane when this solubilizer was not removed from the suspension.

The particles created from PE milk jug pieces (**Figure 4D**) appeared to have a rougher texture in comparison to the commercial PE. Some of these particles were spherical but many were variable in shape. The sM&NP formed from commercially obtained PET were mostly spherical with a wide range of sizes (**Figure 4B**) and were overall larger than the PE particles, in agreement with the particle size analyzer data shown in Tables 1 and 2. The particles created from water bottle PET, solubilized using *n*-dodecane or 2-dodecanone, were fairly uniform in size, but less spherical (**Figure 4E**). Additional images can be found in the supplementary data document. Raman spectral analysis of the larger particles from both samples (**Figure 5B**) confirmed their identity as PET. Aqueous suspensions of PS NP formed from either commercial or real-world sources using *n*-dodecane as the solubilizer were spherical (**Figure 4C, 4F**). Different from PE and PET, the real-world PS particles were consistently observed as spherical.

3.4 Role of the plastic solubilizer

The mechanism for sMP&NP creation utilizing organic solubilizers in water is not yet fully understood. At this point, we posit that the formation of these suspended particles is from the ability of the solubilizer to infiltrate the polymer chains, effectively separating polymer molecules. Upon folding of the individual long chains, mostly spherical shapes are created in water, which may be driven by thermodynamic forces. Literature molecular simulation studies of hydrocarbons in methanol suggest that large hydrophobic molecules fold in order to limit interactions with this polar solvent.(Denayer, Vekeman et al. 2021) However, many non-spherical shapes were also observed in this study, including rod-like shapes that were seen in our real world PE and PET sMP&NP samples. Previous studies have also reported rod or fibrous shapes for weathered PE films created by fragmentation.(Hebner and Maurer-Jones 2020) These comparisons suggest that NP from real world plastics, which undergo further fabrication compared to the commercial source plastics, may form differently shaped sMP&NP in water.

This strengthens the argument that MP and NP made from real world plastics, not just the spherical NP created from commercial products, need to be used in assessing the effects on biological systems.

To further explore the function of the organic solubilizer in the sM&NP suspensions, the added organic was deliberately removed by organic solvent extractions and subsequent heating. After the removal of over 99% of the *n*-dodecane from the aqueous suspension, as measured by SPME/GCMS, the suspension became less cloudy. This treated solution was analyzed with dark field microscopy and 100X images are shown in **Figure 6**. The sMP&NP again were a range of sizes, and observed through image analysis to be smaller than the particles in the presence solubilizer molecules. The notable decrease in the cloudiness of the aqueous suspension corresponds with smaller sized NP; this was observed upon removal of the solubilizer *n*-dodecane from PE and PP suspensions. In real world waters, many nonpolar substances interact with sMP&NP, similar to the organic solubilizers used in these experiments. Among other changes, these organic molecules and other natural water components can aggregate the nanoplastics into larger particles.(Mao, Li et al. 2020, Zhang, Cheng et al. 2022)

We determined that different liquid, paraffin-type compounds, including *n*-undecane, tetradecane, 2-dodecanone, 1-octanol, triacylglycerols and kerosene readily create suspended sMP&NP in water with a range of particle size distributions. Numerous stable sMP&NP suspensions in aqueous media have been created using this methodology from common olefin polymers (PE, PP and Polystyrene) and other widely used condensation polymers (PET, polyamides (nylon), and polycarbonates). We have successfully solubilized a variety of plastic waste to demonstrate the creation of these suspended particles of plastic from aged/used materials. Further, we found that this approach is effective in forming aqueous solutions of sMP&NP from fibrous plastics, such as polyester (PET) fabrics and face mask materials. These aqueous NP suspensions remain stable upon the addition of salts and other dissolved substances, such as biological growth media. These observed properties support the likelihood of sMP&NP formation occurring by this process in real-world water systems.

4. Conclusions

Our experiments demonstrate for the first time that small micro and nanoplastics (sM&NP) can be readily and reproducibly formed in aqueous conditions using agitation and ultrasound mixing of these plastics in the presence of simple organic liquid solubilizers. A number of paraffin-type compounds, including scission products from polymer degradation, can solubilize plastics to form sMP&NP sized particulates that readily suspend and homogeneously distribute in water. The ease of sMP&NP formation in water via this mechanism suggests that these particles will be present in many natural aqueous systems, much more than previously considered, and even may be part of the unaccounted waste plastic in surface waters. This work also suggests that sMP&NP are not solely formed from longer-term weathering of waste plastics. More research is essential for understanding the extent of sMP&NP releases from plastics in contact with water where paraffin-type compounds are present, e.g., following an oil spill.

The particle size distributions of sMP&NP can be tailored by using different plastic feedstocks, solubilizer selection as well as type of mixing (hand-mixing/length of sonication). Thus, this straightforward method for sMP&NP formation in water has the potential to advance future research, notably studies of the human biological responses to these pollutants formed from real-world plastic materials. Serendipitously, this facile formation of sMP&NP suspensions in water may also provide a solution for environmental remediation and the chemical recycling of plastic, which relies on the conversion of polymers back to smaller units, either the original monomers or oligomers for remanufacturing purposes. Since the chemical properties of plastic have traditionally required the use of hazardous solvents, these NP suspensions in water may offer a greener, nonhazardous, environmentally friendly pathway for chemical recycling.

Table 1. Particle size ranges and averages for commercial, real world and aged plastic materials in water after addition of a solubilizer and two minutes of vigorous hand shaking mixing.

Polymer type and description	**Particle size range (µm)**	**Average particle size (µm)**
PE – commercial	0.9-2.0	1.3 ± 0.2
PE – milk jug	1.8-4.9	3.1 ± 0.9
PE – aged real world	1.6-4.9	2.5 ± 0.7
PET – commercial	1.5-4.9	3.4 ± 0.9
PET – water bottle	3.0-5.6	4.4 ± 0.7
PET – aged real world	3.3-5.6	4.4 ± 0.5
PS – commercial	1.3-2.5	1.8 ± 0.6
PS – EPS product	1.4-3.1	2.3 ± 0.5
PS – aged real world	0.9-4.5	2.0 ± 0.7

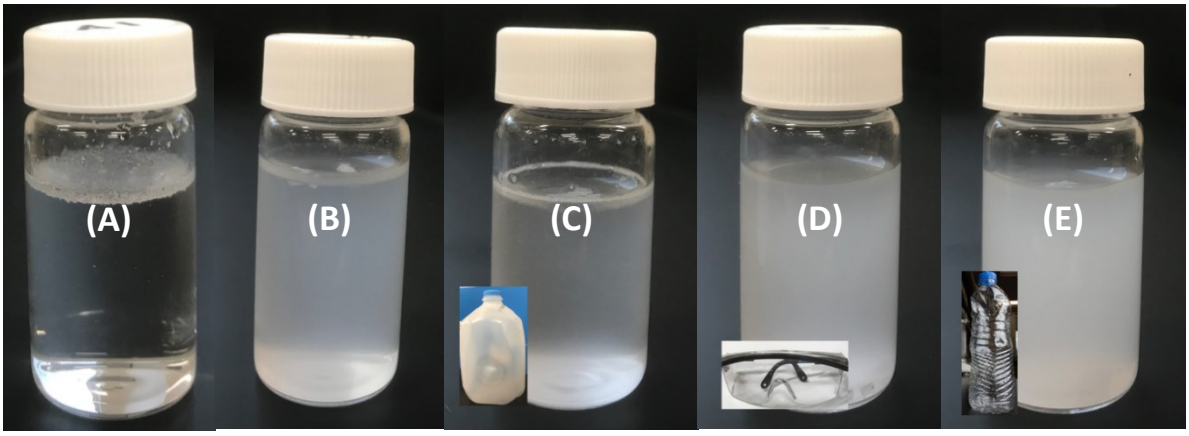


Figure 1. Plastics (10 mg) in 18 mL of water after 30 seconds of vigorous shaking and 30 minutes of ultrasound mixing: **(A)** PE MP in water; **(B)** PE MP in water and 20 µL of *n*-dodecane as the solubilizer; **(C)** a piece of a PE milk jug in water and 20 µL of *n*-dodecane; **(D)** PC shavings from safety glasses and 20 µL of 2-dodecanone as the solubilizer; and **(E)** a piece of PET water bottle and 20 µL of kerosene as the solubilizer.

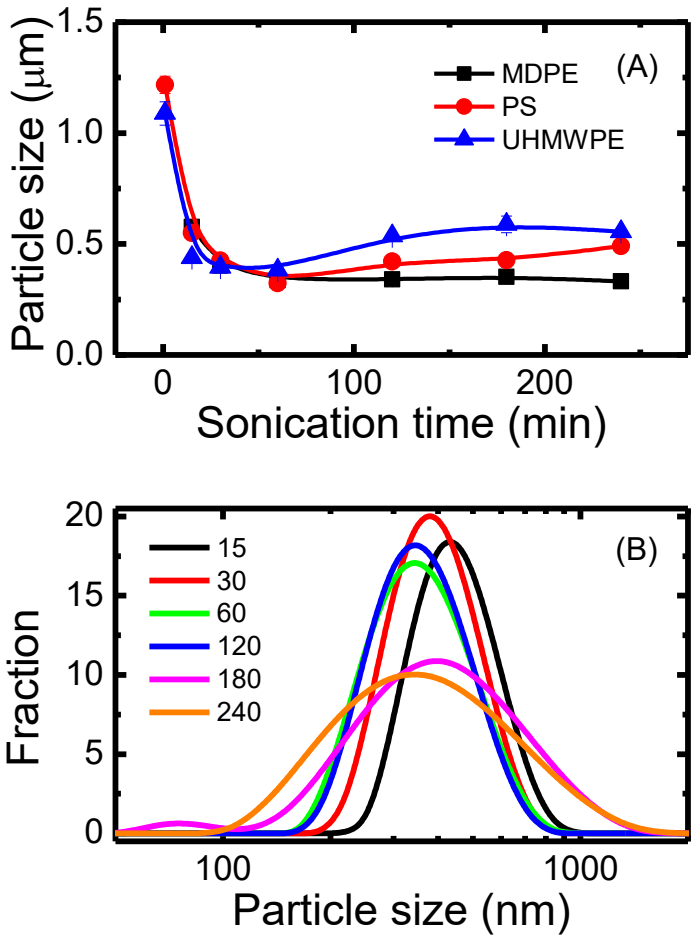


Figure 2. (A) Sonication time dependence for average particle sizes for MDPE (■), PS (●), and UHMWPE (▲) NP in aqueous solution using *n*-dodecane as the solubilizer. **(B)** Specific particle size distributions generated for MDPE as a function of sonication time (min).

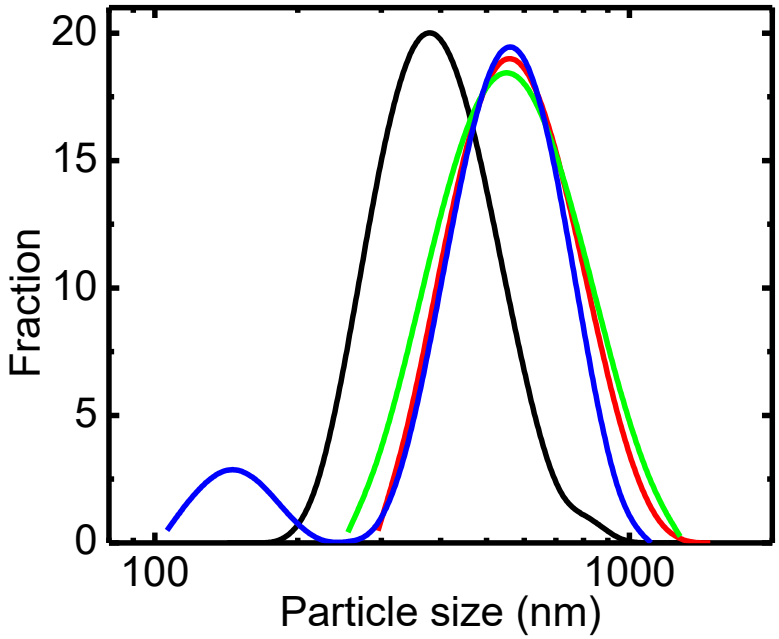


Figure 3. Comparison of commercial MDPE NP particle size distribution (**black**, *n*-dodecane) with real-world milk jug kerosene NP (**red**, kerosene) formation (see also Table S1). The measured distributions of the milk-jug NP left undisturbed (but remixed before measurement) for two (**green**) and three (**blue**) months.

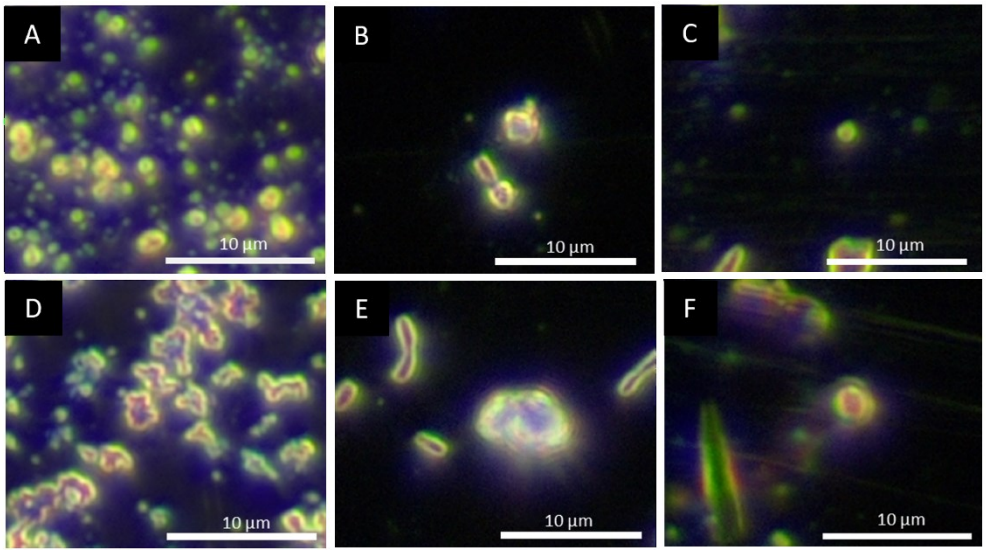
355

356 **Table 2**. Average particle sizes of different plastics after 60 minutes of ultrasound mixing with kerosene

357 or *n*-dodecane as the solubilizer.

Plastic	Solubilizer	NP size, average (nm)
MDPE	*n*-dodecane	338 ± 14
UHMWPE	*n*-dodecane	358 ± 9
Milk-jug PE	kerosene	528 ± 19
PET	*n*-dodecane	724 ± 14
PET	kerosene	516 ± 28
PS	*n*-dodecane	700 ± 13

358



359

360

361 **Figure 4.** Dark field microscopy images of deposited NP from an aqueous solution of suspended

362 commercial PE NP **(A)** PE NP from a milk jug **(D)**, commercial PET NP **(B)**, PET NP from a water bottle **(E)**,

363 commercial PS NP **(C)**, and PS NP from a plastic cup **(F)**.

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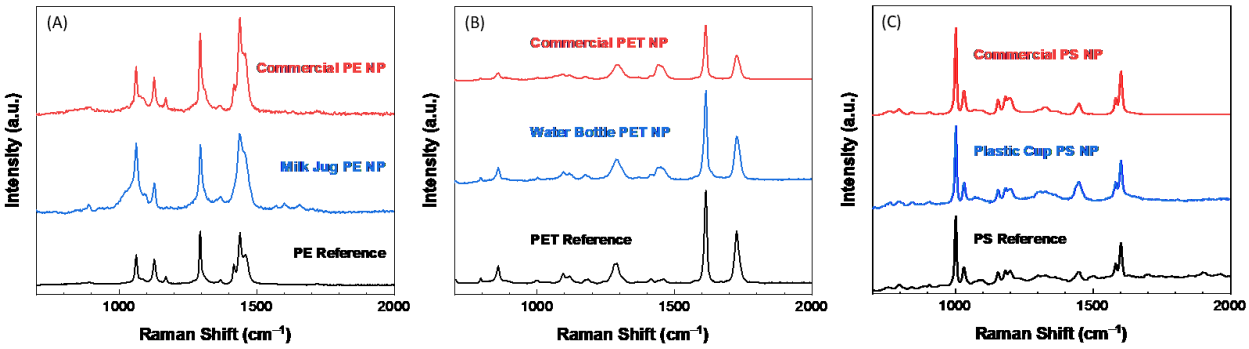
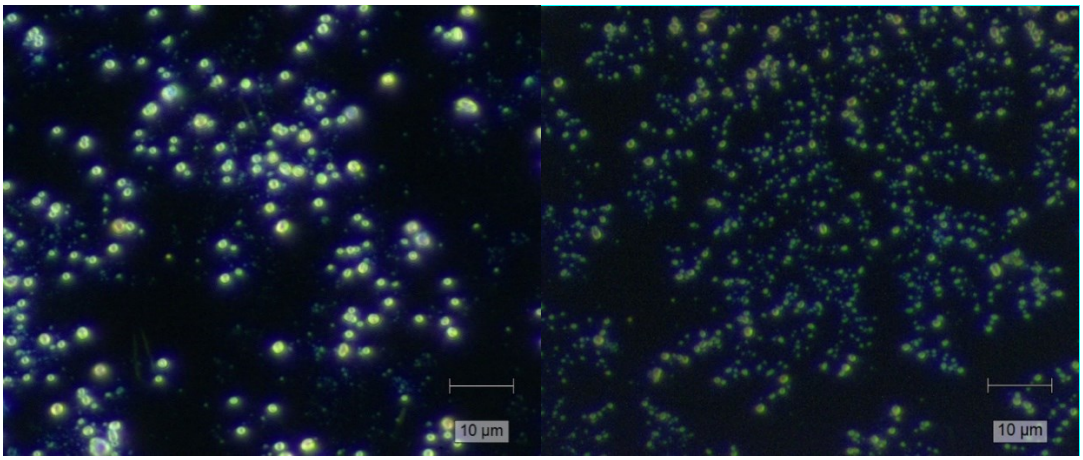


365

366 **Figure 5.** Raman spectra of commercial PE NP, milk jug PE NP, and a PE reference (A), commercial PET

367 NP, water bottle PET NP, and a PET reference (B), and commercial PS NP, plastic cup PS NP, and a PS

368 reference (C).



369

370 **Figure 6.** Dark field microscopy images (100X) of pure PE particles after the removal of *n*-dodecane.

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372

373 **Declarations**

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