Research Square

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Preparation of block copolymer-stabilised microspheres of common polymers and their use as microplastics proxies in degradation studies

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Abstract

The environmental fate and impact of microplastics as well as their possible physiological effects, are expected to depend on their physico-chemical characteristics, including polymer types and surface chemistry. There is thus a clear need to develop a broad range of model microplastic particles to study the fate and effects of environmentally relevant microplastics. Here, a simple one-pot procedure to prepare sub-10 μm poly(ethylene glycol) (MPEG)-stabilised glycol modified poly(ethylene terephthalate) (PETG), poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), polycarbonate (PC) and polycaprolactone (PCL) particles is described. The prepared particles can be dried and directly re-suspended in water, making them easy to handle and relevant mimics of microplastics. In addition the method was extended to prepare somewhat larger polyethylene-based (PE) particles and control PET particles were also prepared.

Selected microparticles were subjected to aerobic biodegradation studies and compared with non-stabilised PET particles. All particles exhibited some degradation. For PLA and PET particles, the degradation corresponded well to the amount of surface stabilising MPEG groups or known impurities, confirming that these polymers do not degrade under the applied conditions but that the stabilising groups do. PCL particles degraded relatively rapidly, consistent with literature data and their relatively small size. PE-based particles degraded more than expected if only degradation of the stabilising groups was taken into account, indicating that the surface chemistry of these particles plays a role in bulk degradation. These studies thus demonstrate the effect of varying the type of polymer and improves the understanding of how surface chemistry affects the degradation of microparticles.

Introduction

Microplastics are ubiquitous in all environmental compartments,(1) giving cause for concern over potential adverse effects.(2–4) As a result of their persistent nature, in combination with a lack of feasible remediation methods, microplastics are expected to accumulate in the environment over time.(5, 6) The degradability of microplastics is, therefore, an area of interest in order to better understand their environmental fate and exposure, ultimately determining their environmental risks.(7, 8) Such information is also relevant when selecting or designing polymers for a specific application, as degradability can be promoted by incorporating specifically unstable bonds or structures that will promote degradability under the required conditions.(9, 10) In the current scientific literature on microplastics, there is a clear overrepresentation of studies using pristine polystyrene microbeads as model test materials.(11–14) At the same time, there is an identified demand for research efforts, dedicated to other plastic types, specifically moving toward microplastics of greater environmental relevance.(14) This is a prerequisite to increase the reliability of risk assessment for microplastics.(15) More environmentally relevant microplastics have been achieved through top-down fragmentation of environmental plastic litter as well as through aging and weathering of commercially available plastics.(14, 16, 17) However, in order to link environmental fate and behaviour to well-controlled modifications of physico-chemical properties, in-house synthesis of model microplastics is considered an advantage. Varying the type of primary polymer of the microplastic particles, enables evaluation of polymer-specific effects from for example swelling, diffusivity, sensitivity to oxidation, exposure to salts, moisture, UV-light and weathering on the behaviour of the microplastic mimics. In addition, it is also essential that the particles are dispersable in water to provide a realistic comparison to microplastics originating from environmental wear, oxidation and hydrolysis. Unless the particles are sufficiently stabilised, while still retaining the fundamental physical properties of the given polymers, it is not pertinent to consider them true mimics of the actual microplastics.

Amphiphilic block copolymers have the ability to stabilise such interphases between hydrophobic polymers and hydrophilic environments, which permits them to function as surfactants(18) for stabilising emulsions, provided that the hydrophobic block and the bulk polymer are highly compatible.(19, 20) For example, Kanakubo *et al.* applied a block copolymer of poly(ethylene glycol) and polylactide (PEG-b-PLA) to prepare water-dispersable particles of poly(lactide-co-glycolide).(21) Traditionally, the preparation of block copolymers requires a significant amount of synthetic work, especially if highly well-defined architectures are required.(22) Such block copolymers will have to be prepared specifically for a given microplastic mimic of interest and then incorporated into the base polymer to ensure formation of particles of the desired size. This relatively large amount of work has traditionally limited the use of block copolymers as particle stabilisers.

Here, we present a simple one-pot procedure to prepare a variety of PEG-stabilised polyesters and polycarbonate particles through an *in-situ* partial transesterification of the polyester or –carbonate with the terminal hydroxy-group of a commercial monomethoxy-poly(ethylene glycol), MPEG in a benign organic solvent.

Subsequent dispersion of the reaction solution into water led directly to an emulsion (in case of a water-immiscible solvent) or a particle dispersion (in case of a water-miscible solvent). Removal of the solvent resulted in microplastic particles with sizes < 10 μm. The produced particles were subjected to aerobic biodegradation studies to gain mechanistic insights into factors influencing their biodegradation as well as document the applicability of the produced model particles in such test systems, relevant to understand their environmental fate. The procedure could also be used to prepare polyethylene particles, although these became larger and less regular in shape.

Results and Discussion

Synthesis of glycol-modified poly(ethylene glycol) (PETG) particles

The initial focus for polyester particles was commercially available glycol-modified poly(ethylene glycol), PETG (Table 1). This copolymer can be considered a non-crystalline PET analogue,(23, 24) and is frequently used as a durable, transparent and inexpensive material in applications where the crystallinity of PET is not desirable. The approach pursued here was that a relatively small fraction of block copolymers of a main-chain polyester or polycarbonate and a hydroxy-terminated water-soluble polymer can be prepared through transesterification (see Scheme 1A). This small amount of amphiphilic block copolymer can then act as a stabiliser of solution droplets or particles upon dispersion into water, depending on the water-miscibility of the solvent used (see Scheme 1C).

Transesterification has been reported using a variety of catalysts.(25, 26) Here, zinc acetate was used due to its low toxicity. Anisole was chosen as a solvent for PETG (as well as for polycaprolactone (PCL), polylactic acid (PLA) and polycarbonate (PC), see below) because it was found to dissolve PETG well at high temperatures, while at the same time having low reported toxicity. In addition, it has a significant vapour pressure despite its relatively high boiling point of 154 ºC. The high boiling point allows conducting the reaction at high temperature, while the high vapour pressure allows relatively efficient removal of solvent residues by reduced pressure at lower temperatures, thus avoiding particle degradation. The direct transesterification with poly(ethylene glycol) monomethyl ether (MPEG) is shown in Scheme 1A.

Initially the rate of transesterification was investigated by size exclusion chromatography using a 1:500 molar ratio between hydroxy groups from MPEG and ester groups (corresponding to 4.4% w/w MPEG). It should be emphasised that all reagents were deliberately used as received, hence some additional hydrolysis may be expected due to residual water content in polymers, catalyst and solvent. In the SEC traces of the sample taken at t = 0 (prior to addition of catalyst, Fig. 1A, black trace), the sharp signal from free MPEG is clearly visible along with the trace of the broad PETG signal. After 1 h most of the MPEG signal has disappeared (Fig. 1A, dark grey trace), although the number average molecular weight of the mixture has not changed significantly (Fig. 1B). These results are consistent with transesterification, since this reaction will not affect the total number of molecules.(27) At longer reaction times, M_n is seen to decrease along with an increase in the MPEG signal, which indicates that concurrent hydrolysis occurs during this period. The exact reason for the delay in hydrolysis was not investigated, but it may be related to the high temperature and low solubility of water in anisole, which reduces the amount of water available for hydrolysis.

After establishing that transesterification was essentially complete in 1–2 hours, the dispersion was effectuated using the setup shown in Scheme 1C; After cooling the polymer solution to 80 ºC, it was transferred into 5 volumes of room temperature water while continuously agitating with a high-speed disperser.

The resulting white dispersion consisted of droplets that were mainly smaller than 10 µm in diameter (see Fig. 2B, top left image). Removal of anisole and water gave PETG particles of comparable size that could be directly redispersed in water (see Fig. 2B, bottom left image).

Particle analysis using both light microscopy and a light scattering method(28) gave comparable results (see Table 2) with no macroscopic precipitation observed, indicating efficient stabilisation and that the image is representative for the entire sample.

Optimisation of stabiliser content

Figure 2A shows the size of dispersed droplets and dried particles as a function of stabiliser content. Below 4.4% w/w MPEG, the particles increase in size and size distribution, which indicates poor stabilisation. On the other hand, further increasing the stabiliser content to 19% w/w (corresponding to an alcohol:ester ratio of 1:100) only leads to a small decrease in the as-dispersed droplet size, whereas the re-dispersed particles appear to be slightly larger. Thus, for preparing small particles while maintaining a significant molecular weight and employing as little stabiliser as possible, the ratio of 4.4% w/w appears to be a good compromise.

Synthesis of particles of poly(ethylene terephthalate), polycaprolactone, polylactic acid and polycarbonate

Following the successful preparation of PETG microparticles, the same procedure was adapted to prepare microparticles of other commonly used polymers. Specifically, polycaprolactone (PCl), polylactic acid (PLA) and polycarbonate (PC) were used as substrates (Scheme 1A), since these polymers were all soluble in refluxing anisole and should in principle be able to undergo transesterification/transcarbonation reaction with hydroxy-groups. In particular, the *molar* ratio between alcohol and ester was kept constant in order to maintain the effect on molecular weight during transesterification. Since the MPEG groups act as stabilisers and thus are predominantly placed on the interface between polymeric and aqueous phase the maximum required stabiliser amount is related to the volume fraction rather than the molar fraction. Therefore, the amount of stabiliser can probably be reduced for most of these polymers, since the molecular weight of the repeating unit is smaller than for PETG while the densities are comparable.

As seen in Fig. 3, PCL, PLA and PC formed spherical, micron-sized droplets with a size comparable to those formed by PETG, illustrating the versatility of the method.

Due to PET not being soluble in anisole, the formation of PET particles was carried out in dimethylsulfoxide (DMSO) instead. Amorphous PET dissolves easily in DMSO near the boiling point, but eventually precipitate at lower temperatures. However, it is desirable to cool the reaction mixture below the boiling point of water to avoid hazardous over-heating during the subsequent mixing step. In addition, DMSO is miscible with water, which means that particles, rather than dispersed droplets, are formed immediately. At 150 ºC the dissolved PET did not precipitate from solution. Relatively slow transfer of this heated solution into excess water under the action of a high speed disperser led to particle formation. As seen in Fig. 3, Fig. 4 and Table 1, the resulting particles are on average less than 2 µm and easily redispersed.

Table 1
Details on synthesized particles.

Name	Added MPEG % w/w	Measured MPEG % w/w[a]	M_n g/mol [b]	Đ [b]	T_g ºC	T_C ºC	w_C % [c]	D_{Micro} µm [d]	D_{NC} µm [e]
MPEG-PETG	4.4	3.4	17,000	1.62	87	-	0	2.7 ± 0.6	2.5
MPEG-PET	5.0	2.6	N/M	N/M	59	250	20[f]	1.4 ± 0.08	1.5
MPEG-PCL	8.7	6.5	13,200	1.44	-43	55	69	2.7 ± 0.8	1.9
MPEG-PC	4.2	2.3	11,100	1.82	118	-	0	5.9 ± 3.4	2.0
MPEG-PLA	13	11	13,300	1.53	40	145	25	3.0 ± 1.5	1.5
MPEG-PE	18	1.3	N/M	N/M	N/M	98	37	22 ± 15	3.9
PET, No Stabiliser	0	9.0[g]	N/M	N/M	98	256	40 [f]	2.0 ± 1.1	3.2

[a] Measured by ^{1}H NMR. [b] Measured by SEC relative to polystyrene standards. [c] Determined as measured peak enthalpy divided by standard polymer heat of fusion according to literature.(29) [d] Diameter of particles dried and redispersed in water, analysed using optical microscope. The standard error is given as the uncertainty. [e] Diameter of particles dried and redispersed in water, analysed using a Nanocuvette™ S. [f] Crystallinity determined using modulated DSC. [g] This value corresponds to residual DMSO as measured by ^{1}H NMR

Synthesis of polyethylene (PE) particles

Polyethylene is one of the most common commodity plastics, and hence PE-based microparticles are of significant interest as a model microplastic.(30) Polyethylene is of course a polyolefin and not a polyester, why the method presented here is not directly applicable. However, the use of commercially available polyethylene grafted with maleic anhydride (MA-PE) should allow attachment of stabilising MPEG functionalities through reaction between anhydride and alcohol (see Scheme 2B).

The MA-PE used has an acid number of around 6 mg KOH /g according to the manufacturer, which corresponds to around 10^{-4} mol acid/g. Since two acids make up one anhydride, MPEG was added stoichiometrically to the anhydride as $5{\cdot}10^{-5}$ mol hydroxy groups, corresponding to 18% w/w (see Table 2). In this case no catalyst was used and the reaction was carried out in refluxing toluene rather than anisole. The reaction mixture was readily dispersed into ethanol to give discrete particles. The ethanol was then exchanged with water, which led to rapid creaming of the MPEG-PE particles with lower density than water. As seen in Fig. 3, Fig. 4 and Table 1, the resulting particles are significantly larger than observed for particles based on the polyesters and also appear to aggregate more. The light scattering results shown in Table 1 appears to contradict this, but this is probably a consequence of the size of the particles; the larger particles rapidly rises, effectively removing them from the light path. As a consequence, only a small amount of well-dispersed particles dispersed are analysed. It should be noted that a control experiment omitting the MPEG led to macro-phase separation and essentially no discrete particles, indicating the importance of the stabilising groups being present.

Analysis of the resulting particles by ^{1}H NMR (see supporting information) reveals that the actual MPEG content is significantly lower compared to the targeted amount at only 1.3% w/w (see Table 2). This low MPEG content indicates either poor reaction efficiency or low stability of the resulting ester bond and probably explains the larger particles observed. The particles were nevertheless included in the present study because of the wide-spread use of PE.(30) If hydrolysed, the anhydride contributes with carboxylic groups in addition to the MPEG stabilising groups, and this distinguishes these particles from ‘pristine’ polyethylene particles. These may, if neutralised, contribute to charge-stabilisation of the particles. In addition, such carboxylic groups are found in polyethylene exposed to UV irradiation(31) and are therefore likely to be found in environmentally generated microplastics. The acid groups may act as a substrate for CoEnzyme A,(31) why these particles are likely to be more prone to biotic degradation than untreated polyethylene.

Synthesis of PET particles without stabiliser

In order to compare the influence of stabiliser on degradation, PET particles without a stabiliser were synthesised. As the role of the stabiliser generally is to prevent particle fusion, preparing comparable particles without stabiliser is not straightforward, although there are literature examples such as using trifluoroacetic acid as a volatile stabiliser(32) or through extensive milling.(33) However, both these methods have drawbacks: Trifluoroacetic acid is a strong acid, which sets demands on equipment, especially if large amounts of particles must be prepared and in addition it may react with the polyester leading to end-group functionalisation,(34) which alters the polymer composition somewhat. On the other hand, milling leads to formation of micron-sized particles but the preparation of particles with a comparable size to those reported here requires extended milling times of around 8 hours,(33) which will probably lead to some amount of polymer degradation.

Here we found that cooling a 10% w/v solution of an amorphous PET film dissolved in DMSO to room temperature led to the formation of a precipitate of crystalline PET particles with sizes comparable to those obtained from the use of MPEG as a stabiliser when redispersed in water (see Table 1 and Fig. 4). This procedure was found to work well for PET, but not for any of the other polyesters. The particle formation is presumably driven by the poor solubility of crystalline PET in DMSO at room temperature, which is emphasised by the relatively high degree of crystallinity of these particles compared to those prepared using the stabiliser (40% vs 20%. See Table 1). In the former case, the amorphous part of the PET is plasticised by DMSO and may reorganise to form crystals, whereas the stabilised particles are quickly dispersed into water, which is a non-solvent to both amorphous and crystalline PET. As a consequence, crystals have a lot less time to form, leading to a lower degree of crystallinity.

The resulting particles were found to have less than 10% residual DMSO (see Table 1) as determined by ^{1}H NMR.

Aerobic biodegradation

Selected polymer particles were chosen for the study of aerobic biodegradation in seawater. In particular, PET particles prepared with and without stabiliser were chosen to assess possible effects of the stabilising groups. In addition, PCL was chosen as a degradable polyester known to degrade under these conditions,(35) whereas PLA was chosen as an aliphatic polyester, known to be biodegradable under industrial composting conditions but not to degrade under aerobic aqueous conditions.(36) Finally the biodegradation of stabilised PE particles was investigated due to the extended use of this polymer and consequently high occurrence in the environment.(37)

Figure 5A shows the degradation results after 2 and 4 weeks. The positive controls, sodium acetate and microcrystalline cellulose degrades as expected, which confirms that the microorganisms are active. For the PET particles with and without stabiliser, as well as for the stabilised PE particles and the stabilised PLA, some degradation is apparent, which at a first glance is surprising as neither of these are expected to degrade under the conditions employed. On the other hand, the stabilised PCL particles degrade as expected (although the value after 15 days has been omitted because the maximum capacity of 80 mg/L BOD of the system is exceeded).(36)

Since the MPEG stabiliser is situated mainly on the particle surface, it is the degradation of this entity that is observed on the otherwise non-degradable particles, since microbial degradation of MPEG is well known.(38) In order to examine this hypothesis, the data in Fig. 5B shows the biodegradation assuming that only the MPEG (where present) contribute to the theoretical oxygen demand. For the MPEG-stabilised PET and PLA, the observed degradation correlates well with the maximum calculated ThOD for the MPEG only (Red line in Fig. 5B), which supports that at least for these two sets of measurements, MPEG degradation is observed, whereas the bulk of the polymer mostly remains unaffected.

Similarly the apparent degradation of the non-stabilised PET particles corresponds well with the residual DMSO content.

As shown in Fig. 5A, MPEG-PE particles show a small, but significant, biodegradation. This degradation is not entirely due to the presence of MPEG groups on the surface, since the actual degradation is significantly larger than what can be explained by MPEG alone (Fig. 5B). However, as mentioned above, biotic degradation of polyethylene has been reported to be promoted by the presence of carbonyl groups,(31) indicating that it is the presence of functional groups on the polymer backbone that makes these polyethylene particles more prone to degradation.

Further insight into the degradation behaviour can be obtained by considering the entire time series in Fig. 6. In the first two days, low activity is observed for all polymers, where the biodegradation for all polymers except for MPEG-PE have very similar values. Such lag phases have been explained by adaptation of the microorganisms to produce enzymes that can depolymerise the particles.(36) After two days, degradation of MPEG-PCL commences, eventually reaching around 40% degradation at 15 days. It is worth noting that this is significantly faster than comparable data for particles with sizes above 100 µm previously reported.(36) As such it is consistent with smaller particles degrading faster due to their larger surface area, although the MPEG surface groups and differences in microorganisms are also likely to have an influence.

Summary and conclusions

A simple one-step procedure has been established as a general procedure for preparation of a range of stabilised polyester microplastics. Surface functionalisation with a short MPEG enabled direct re-dispersion in water as well as sufficient stability in water to enable handling in aqueous media without substantial creaming or precipitation. Through this simple process, it was possible to prepare sub 10 µm spherical particles of a

range of the most commonly used polyesters, PETG, PLA, PCL and PET as well as of a polycarbonate, PC. In addition the process was extended to preparation of PE microplastic particles by modification of a maleic acid functional PE, although these became larger and were more irregular in shape. Particles of the more commonly used polymers were evaluated in biodegradation tests and the impact of both surface functional groups as well as the type of polymer was evaluated. Since the method permits a broad use of different parent polymers, and could be extended to different surface groups, it is possible to prepare microparticles mimicking the actual bulk- and surface chemistry of microplastics found in nature. We therefore consider the method of high value for preparation of realistic microplastics for laboratory screening and testing, where also the polymer properties can be taken into account to elucidate this important field.

Materials and methods

Materials

Poly(lactic acid) (PLA) was a Natureworks 2003D thermoplastic resin. Polycarbonate (PC) was an unlabelled sample, with the identity confirmed by ^{1}H NMR ($CDCl_3$). Polycaprolactone (PCl) was a CAPA6500 thermoplastic resin acquired from Perstorp. Poly(ethylene terephthalate) (PET) was a PET FlexPET F-PAP film obtained from DanaPak Flexibles, with the identity confirmed by ^{1}H NMR ($CDCl_3$:trifluoroacetic acid 5:1). Poly(ethylene terephthalate), glycol modified (PETG) was a poly(ethylene-*ran*-neopentyl terephthalate) Selenis Bondz GG074 copolymer acquired from Selenis. All polymers were used as received without any prior drying.

Polyethylene-*graft*-maleic anhydride (PE-g-Mal, 500 cP at 140 °C), Poly(ethylene glycol) methyl ether, M_w = 5000 ($MPEG_{113}$-OH), anisole (99%), deuterated chloroform (CDCl3, 99.8% D), trifluoroacetic acid (TFA, 99%), dimethyl sulfoxide (DMSO, > 99.5%) and zinc acetate dihydrate ($Zn(OAc)_2.2H_2O$) was acquired from Merck and used as received.

Samples of activated sludge was collected from Mølleåværket wastewater treatment plant (Lundtofte, Denmark) and used as inoculum in the biodegradation tests. Biodegradation tests were carried out using OxiTop® instrumentation (WTW).

Table 2
Data of starting materials

Manufacturer designation	Description	Abbreviation	Manufacturer info	M_n / g/mol [a]	M_w/M_n [a]	T_G / °C [b]	T_C / °C [b]	Peak Enthalpy, 1st heat / J/g [b]	Crystallinity [b] / % [b]
	Poly(ethylene glycol methyl ether	MPEG-OH	M_n = 5,000	8,400	1.10	N/A[c]	63	199.9	100
PETG17505191025B	Poly(ethylene terephthalate glycol-modified)	PETG		28,000	1.97	73	N/C	N/C	N/C
1_PC_144R	Polycarbonate	PC		23,600	1.91	144	N/C	N/C	N/C
Perstorp CAPA 6500	Polycaprolactone	PCl		56,000	1.86	-61	62	86.1	64
2003_D_PLL	Poly(lactic acid)	PLA		98,000	1.41	64	154	35.9	38
PET Film	Poly(ethylene terephthalate)	PET		N/M	N/M	76	254	15.5	11 [d]
	Polyethylene-graft-maleic anhydride	PE-g-Mal	500 cP, 140 °C Saponification: 3–6 mg/g	N/M	N/M	N/M	99	111.0	38

[a] THF SEC using polystyrene standards [b] measured by DSC. [c] The material was highly crystalline and showed no apparent glass transition [d] Assuming no cold crystallization. N/M : Not measured due to solubility or cooling limitations

Methods

General procedure for preparation of particles through transesterification of polyester or polycarbonate and monomethoxy polyethylene glycol (MPEG)

In a general procedure, 1 g polyester or polycarbonate was mixed with MPEG-OH, keeping a fixed molar ratio between terminal hydroxy-groups and ester/carbonate groups for all polymers (see text for details). To this mixture was added $Zn(OAc)_2.2H_2O$ (1% mol/mol relative to ester groups) and 5 mL anisole.

The mixture was heated to reflux to dissolve. After 1 h, the resulting solution was allowed to cool to 80 ºC. When the temperature was reached, the mixture was dispersed into approximately 5 volumes of water using an ultraturrax high speed disperser.

The resulting dispersion was evaporated on a rotary evaporator to remove the majority of organic solvent. The remaining particle-dispersion was freeze-dried to isolate particles in 60–70% yield.

The procedure could be scaled up to at least 100 g without issues, simply by scaling all components. Test experiments indicate that solvent can be removed by drying methods such as e.g. spray-drying.

Preparation of MPEG-PETG particles

PETG (100 g, 0.46 mol ester groups), MPEG-OH (4.6132 g, 0.92 mmol hydroxy-groups) and zinc acetate dihydrate (1.0234 g, 4.7 mmol) was dissolved in anisole (500 mL, 497 g, 4,6 mol) in a 1 L jacketed reactor with overhead stirring, by heating to reflux.

The reaction mixture was heated overnight after which the temperature was reduced to 80 ºC. The resulting solution was transferred through the bottom outlet of the reactor to 2.5 L liter water at room temperature, while agitating using an 'Ultra-Turrax' disperser and the reactor was washed twice with 50 mL anisole, which was added to the dispersion.

Approximately one third of the solution was evaporated on a rotary evaporator at 50 ºC, while applying a vacuum of 10–15 mbar.

The particles could be isolated through freeze-drying or through spray-drying.

Isolated yield: Approximately 70–80 g (this batch was used to test various purification methods, why the yield is estimated, and may not be representative)

Preparation of MPEG-PCl particles

In a 25 mL round-bottom flask was added PCL (1.0301 g, 9.0 mmol ester groups), MPEG-OH (0.0883 g, $1.77 \cdot 10^{-5}$ mol hydroxy groups) and anisole (5 mL). To this mixture was added zinc acetate dehydrate (0.0212 g, $9.66 \cdot 10^{-5}$ mol). The flask was fitted with a condenser, filled with nitrogen placed on a hot-plate using a 'DrySyn' heating block and heated to reflux (temperature set to 165 ºC) under nitrogen. After 30 h, the reaction mixture was cooled to 80 ºC and dispersed into 40 mL water at room temperature while agitating using an 'Ultra-Turrax' disperser. Approximately one third of the solution was evaporated on a rotary evaporator at 50 ºC, while applying a vacuum of 10–15 mbar. The particles were isolated through freeze-drying. Isolated yield: 0.48 g.

Preparation of MPEG-PC particles

In a 25 mL round-bottom flask was added PC (1.0152 g, 4.0 mmol carbonate groups), MPEG-OH (0.0415 g, $8.30 \cdot 10^{-6}$ mol hydroxy groups) and anisole (5 mL). To this mixture was added zinc acetate dehydrate (0.00837 g, $3.81 \cdot 10^{-5}$ mol). The flask was fitted with a condenser, filled with nitrogen placed on a hot-plate using a 'DrySyn' heating block and heated to reflux (temperature set to 165 ºC) under nitrogen. After 20 h, the reaction mixture was cooled to 80 ºC and dispersed into 50 mL water at room temperature while agitating using an 'Ultra-Turrax' disperser. Approximately one third of the solution was evaporated on a rotary evaporator at 50 ºC, while applying a vacuum of 10–15 mbar. The particles were isolated through freeze-drying. Isolated yield: 0.82 g.

Preparation of MPEG-PLA particles

In a 25 mL round-bottom flask was added PLA (1.0101 g, 14.0 mmol ester groups), MPEG-OH (0.1401 g, $2.80 \cdot 10^{-5}$ mol hydroxy groups) and anisole (5 mL). To this mixture was added zinc acetate dehydrate (0.03485 g, $1.59 \cdot 10^{-4}$ mol). The flask was fitted with a condenser, filled with nitrogen placed on a hot-plate using a 'DrySyn' heating block and heated to reflux (temperature set to 165 ºC) under nitrogen. After 20 h, the reaction mixture was cooled to 80 ºC and dispersed into 50 mL water at room temperature while agitating using an 'Ultra-Turrax' disperser. Approximately one third of the solution was evaporated on a rotary evaporator at 50 ºC, while applying a vacuum of 10–15 mbar. The particles were isolated through freeze-drying. Isolated yield: 0.76 g.

Preparation of PEG-stabilised PE particles

Me-PEG_{113}-OH (0,2129 g, $4{,}26 \times 10^{-5}$ mol OH), and PE-g-Mal (1,006 g, ~$1{,}1 \times 10^{-4}$ mol maleic anhydride) was placed in a 25 mL round-bottom flask with a magnetic stir bar. 5 mL toluene was added, the flask was fitted with a reflux condenser and the solution was heated to reflux under nitrogen.

After 20 h, the solution was cooled to 60 ºC and water (0,02 mL, 0,02 g, $1{,}1 \times 10^{-3}$ mol) was added and the reaction was left for further 4 hours.

After 4 hours the mixture was dispersed into 50 mL ethanol using an Ultraturrax high-speed disperser.

The resulting particles were allowed to settle and the excess ethanol was decanted off. Then further 5 mL ethanol was added, the dispersion was treated with the ultraturrax and again allowed to settle, followed by decanting off excess ethanol. Finally, 50 mL water was added, which led to rapid creaming of the less dense polyethylene particles. The creamed particle phase was then freeze-dried. Isolated yield: 0.40 g

Preparation of PEG-stabilised PET particles

PET (1,01 g, 5,27 $x10^{-3}$ mol ester) was mixed with Me-PEG_{113}-OH (0,0537 g, 1,07$x10^{-5}$ mol OH), $Zn(OAc)_2.2H_2O$ (0,011 g, 5,01$x10^{-5}$ mol) and 5 mL DMSO.

The mixture was heated to reflux for 5 h under nitrogen, which led to formation of a uniform solution. Then, further 5 mL DMSO was added, and the temperature was reduced to 150 ºC. At this temperature the solution was poured into 5 volumes of water while agitating using an ultraturrax disperser. The particles were left to settle and the top layer was carefully poured off.

The resulting particles were dispersed into 100 mL ethanol on a magnetic stirrer and then left to settle, followed by careful removal of the ethanolic liquid phase. The particles were then dispersed into 50 mL water on a magnetic stirrer. The water was carefully removed after settling. Then the particles were freeze-dried. Isolated yield: 0.71 g.

Preparation of non-stabilised PET particles

A PET film (27,40 g) was mixed with 260 mL DMSO and heated to 180 ºC for 5 h to dissolve completely.

After cooling to room temperature, 400 mL water was added to the resulting gelly material and treatment for 5 minutes with an ultraturrax high speed dispersed gave particles. The particles were filtered on a glass filter, washed with water and dried.

Isolated yield: 6.59 g

Size Exclusion Chromatography

Size exclusion chromatography of PETG, PCL, PLLA, PC and PEG was carried out on a chromatographic system consisting of a Waters Acquity solvent delivery module and column oven, connected to a Waters PDA TS detector and Malvern Omnisec Reveal triple detector array (RI, light scattering, viscometer). The columns were a 150 x 4.6 mm Acquity APC™ XT 450 2.5 µm, a 150 x 4.6 mm Acquity APC™ XT 200 2.5 µm and a 150 x 4.6 mm Acquity APC™ XT 45 1.7 µm organic size exclusion chromatography columns connected in series. All samples were analyzed using a flow rate of 0.7 mL/min in stabilized tetrahydrofuran at 35°C.

PC, PCL and PEG were dissolved in THF at a concentration of approximately 5 mg/mL. PETG and PLL are poorly soluble in THF, why they were dissolved in CH_2Cl_2 at the same concentration but eluted in THF. 10 µL was injected of each sample after filtration through a 0.45 µm PTFE filter.

Nuclear Magnetic Resonance

^{1}H Nuclear magnetic resonance spectroscopy of PET, PETG, PLLA, PCl and PC particles was performed on a Bruker 300 MHz spectrometer at ambient temperature. All spectra were acquired using 128 scans. PETG, PLLA, PCL and PC particles were dissolved in $CDCl_3$. PET particles were dissolved in a 6:1 v/v mixture of $CDCl_3$ and trifluoroacetic acid. Concentrations were around 40 mg / mL for all samples

^{1}H Nuclear magnetic resonance spectroscopy of PE particles was performed on a Bruker AVANCE 600 MHz spectrometer at 120 ºC in deuterated 1,1,2,2-tetrachloroethane (dTCE) at a concentration of 40 mg/mL. Samples were prepared by mixing PE and solvent in an NMR tube, heating to 120 ºC until dissolved. After transfer to the instrument, the sample was equilibrated at 120 ºC before spectra were obtained.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed on a Discovery DSC (TA Instruments, DE, USA). DSC measurements were carried out from − 90°C to 200°C for PCL, PLA, PC and PE and 290°C for PETG and PET, at a heating rate of 10°C min-1 under nitrogen atmosphere. Afterwards, the DSC curves were analyzed by using TRIOS TA instruments software.

Modulated DSC (mDSC) measurements on PET was carried out from 20 ºC to 300 ºC using a heating rate of 5 ºC / min with an amplitude of 0.53 ºC and a period of 40 s.

Microscopy

Bright field microscopy images were acquired using a Leica DM L microscope fitted with a LEICA MC 190HD Camera. LAS EZ Leica Application Suite Vs 3.4.0 Bld: 272 was used for acquiring and calibrating images.

Particle sizes were measured using the 'Analyze Particles' function in ImageJ after defining the scale, converting the image to a grey-scale image and adjusting the threshold to ensure high contrast between particles and background. The size range used was 0.5 µm to Infinity, with any value

of circularity and with exclusion of particles on the edge of the image.

Dynamic Light Scattering/Nanocuvette

Light scattering measurements were carried out using Nanocuvette™ S cuvettes in combination with a Shimadzu 1900i UV-Vis spectrophotometer. This measurement principle is based on measuring diffusion measurements using a photonic crystal.(28)

Aerobic biodegradation

The aerobic biodegradation was assessed using as inoculum activated sludge at low concentration (30.25 mg/L, see Eq. 1) of total suspended solids, TSS, from the Lundtofte wastewater treatment plant (Kgs Lyngby, Denmark). In this experiment, 100 mg/L (36.5 mg/bottle) of material was added in the corresponding bottles except in the inoculum blanks where only the inoculum and the nutrients were added. The total volume of inoculum and test medium added up to 365 mL to ensure good stirring and enough headspace for oxygen transfer (aerobic). This headspace results in a BOD capacity of 80 mg/L.

The theoretical oxygen demand (ThOD) is calculated based on the oxygen needed to convert the organic carbon in the samples to CO2 based on the chemical formula of the polymers and Equation S 2. Calculated ThOD values can be seen in Table S1.

Biodegradation was determined by measuring the oxygen demand in a closed respirometer following ISO 14851. The biochemical oxygen demand (BOD) was calculated from the change in pressure caused by carbon dioxide evolution by test material degradation in the closed bottles. The pressure change was determined using OxiTop® (WTW, Germany) measuring heads.

The percentage of biodegradation is based on the measured BOD versus the ThOD i.e. Biodegradability (%) = BOD/ThOD × 100.

The reaction vessels were prepared approximately 50 h after the inoculum collection. The inoculum was constantly aerated during this period. In total, 22 flasks were prepared for the experiment, with triplicates for all test samples and inoculum blank, and duplicates for the reference materials (Table S2). The test media was prepared from standard nutrient solutions (ISO 14851:2019, 2019).

After adding material, test medium and inoculum, a carbon dioxide absorption tube containing two NaOH pellets was inserted in each bottle, and these were closed tightly before being placed on a stirrer platform and incubated at constant temperature (20 ºC) and under stirring with magnetic bars (180–450 rpm) for 28 days.

$$TSS\left[\frac{g}{mL}\right] = \frac{1}{3} \bullet \left(\sum_{i=1}^{3} \frac{m_{drysludge}}{V_{sludge}}\right)$$

$$TSS\left[\frac{mg}{bottle}\right] = TSS\frac{mg}{mL} \bullet x\frac{ml}{bottle}$$

$$TSS\left[\frac{mg}{L}\right] = TSS\frac{mg}{bottle} \bullet \frac{1}{0.365}\frac{bottle}{L}$$

$$x = 3.2\frac{ml}{bottle}; Itcanvarybasedonthedesiredconcentrationof TSS.$$

Equation 1: Calculation of Total Suspended Solids, TSS

$$npolymerunit + nO_2 \rightarrow nH_2O + nCO_2$$

$$m_{O_2} = n_{O_2} \bullet M_{O_2}$$

$$m_{polymerunit} = n_{polymerunit} \bullet M_{polymerunit}$$

$$ThOD_{calculated} = 100\frac{mg}{L} \bullet \frac{m_{O_2}}{m_{polymerunit}}$$

Equation 2: Calculation of Theoretical Oxygen Demand (ThOD)

Abbreviations

BOD	Biochemical Oxygen Demand
$CDCl_3$	Deuterated Chloroform
DMSO	Dimethyl sulfoxide
D_{NC}	Particle Diameter determined using a Nanocuvette™ S
DSC	Differential Scanning Calorimetry
IFD	Innovationsfonden
KOH	Potassium Hydroxide
MA	Maleic Anhydride
MCC	Microcrystalline Cellulose
MPEG	Monomethoxy polyethylene glycol
$MPEG_{113}$	Monomethoxy polyethylene glycol with ethylene glycol degree of polymerisation of 113
MPEG-OH	Monomethoxy monohydroxy polyethylene glycol
NMR	Nuclear Magnetic Resonance
PC	Polycarbonate
PCL	Polycaprolactone
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PETG	Glycol-modified poly(ethylene glycol)
PLA	Polylactic acid
PTFE	Polytetrafluoroethylene
RI	Refractive Index
SEC	Size Exclusion Chromatography
T_C	Crystallisation Temperature
TCE	1,1,2,2-Tetrachloroethane
TFA	Trifluoroacetic acid
T_G	Glass Transition Temperature
ThOD	Theoretical Oxygen Demand
THF	Tetrahydrofuran
TSS	Total Suspended Solids
UV	Ultraviolet

Declarations

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Contributions:

JM developed the preparation and analysis of the analysed polymer microparticles and was a major contributor to the data treatment and in writing the manuscript. AR performed biodegradation experiments and contributed to the data treatment. NBH was a major contributor to the data treatment of the biodegradation data and in writing the manuscript. AED was a major contributor to the interpretation of the data and in writing the manuscript.

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Ethics declarations

Ethics approval and consent to participate: Not applicable (No experiments were conducted on animals nor humans.)

Consent for publication: All authors consent to publication

Competing interests: The authors declare no competing interests.

Supplementary information

Availability of data and materials: The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. The supplementary information includes the raw respirometer data from the biodegradation experiments, the spectral data from the nanocuvette (including reference spectra), DSC data in trios format, NMR spectra reproduced in a word document and collected in a MestreNova file, along with size exclusion chromatograms shown in a word document. Microscopy images are shown in the main text. Should any raw data files be needed in another format, they are available from the corresponding author upon reasonable request.

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures

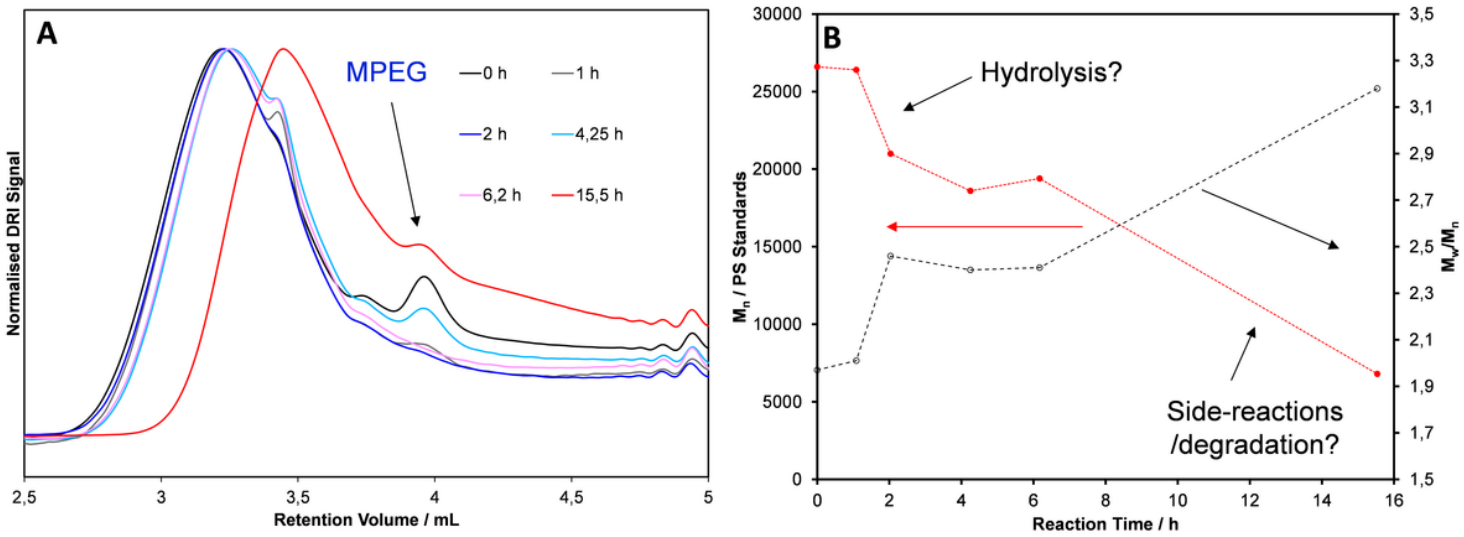

Figure 1

Reaction between MPEG and PETG: Influence of reaction time on molecular weight and distribution A) Size exclusion chromatograms of reaction mixtures taken at various times. B) Evolution of number average molecular weight and dispersity with reaction time

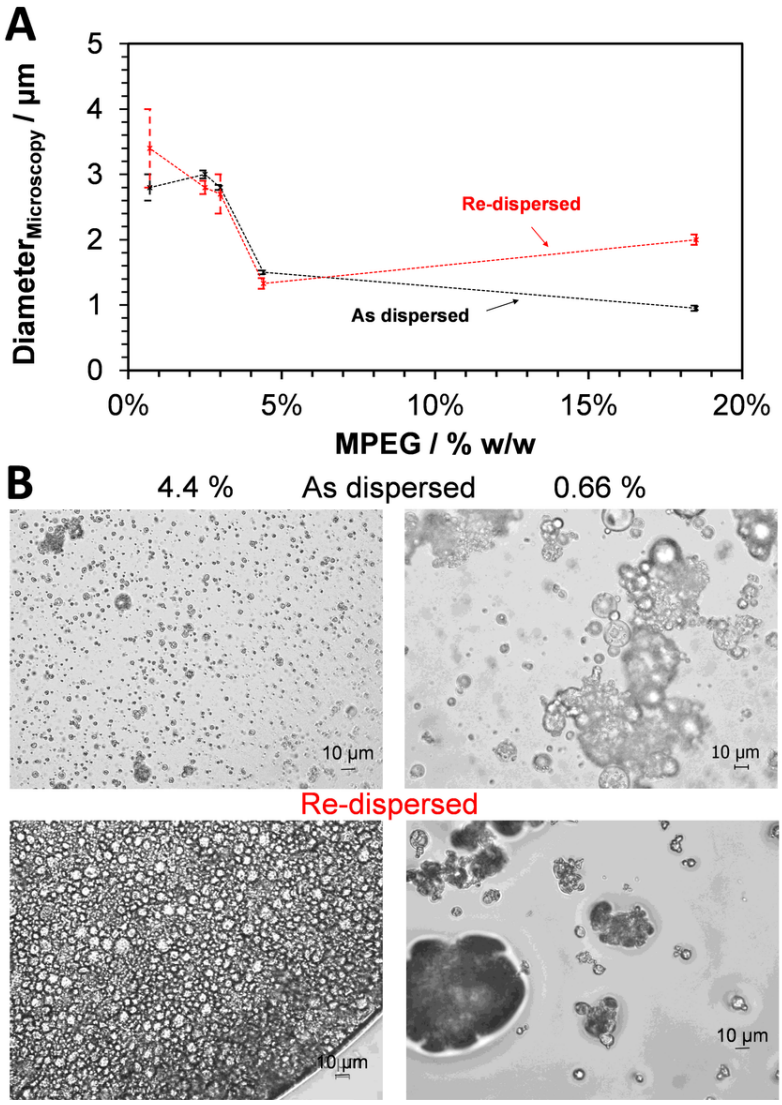

Figure 2

A) Particle size of PETG as a function of added MPEG content after transesterification in anisole determined using optical microscopy. As dispersed samples are the droplets directly obtained from dispersion without drying, whereas the re-dispersed sample set designates particles that have been dried and redispersed in water. B) Microscopy images of as dispersed (top) and re-dispersed (bottom) transesterified samples of 4.4 % w/w and 0.66 % w/w added MPEG-OH. The scale bar of all images is 10 µm.

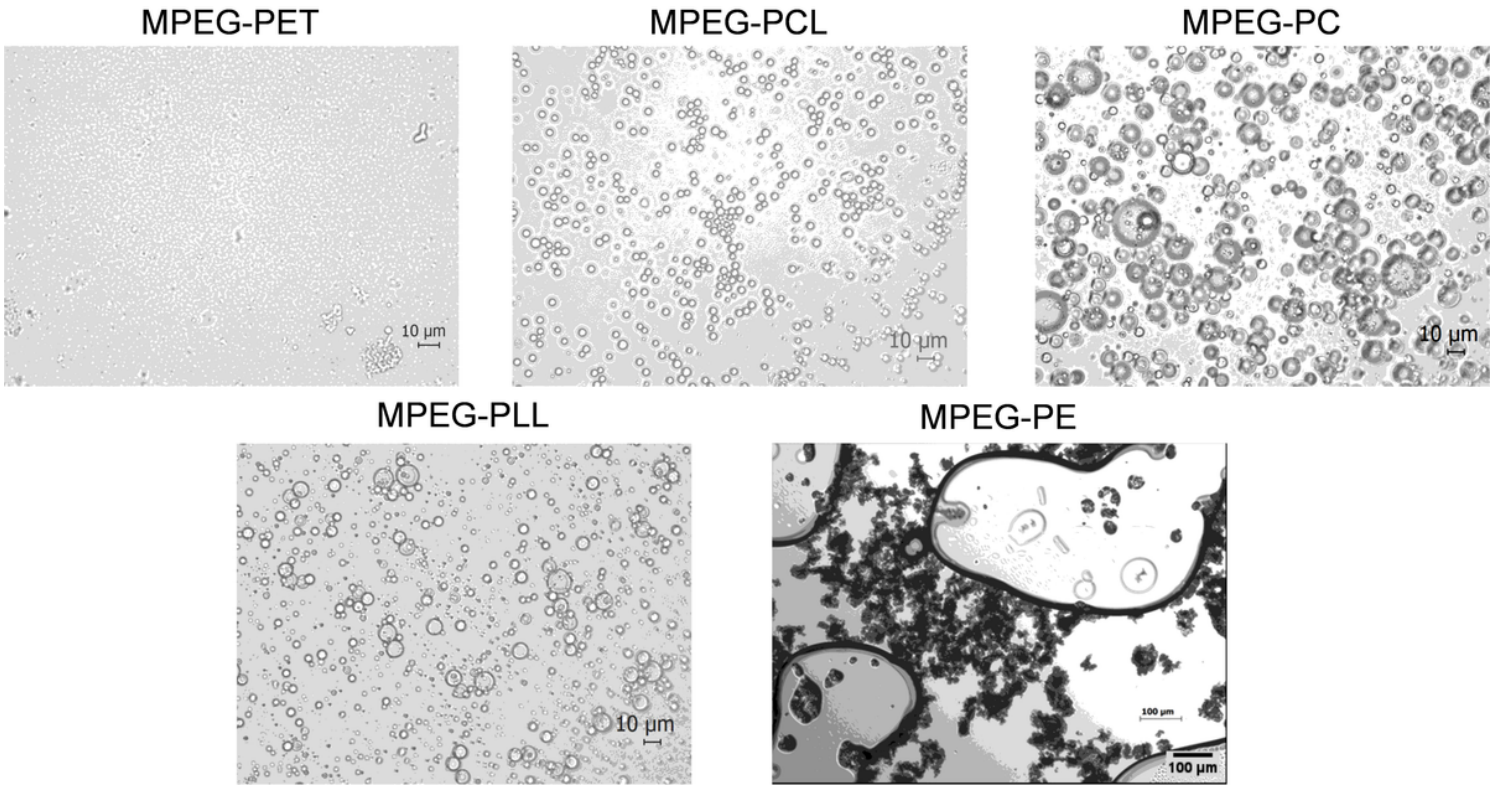

Figure 3

Microscopy images of as-dispersed particles/droplets. Note the different scale-bar for PEG-PE

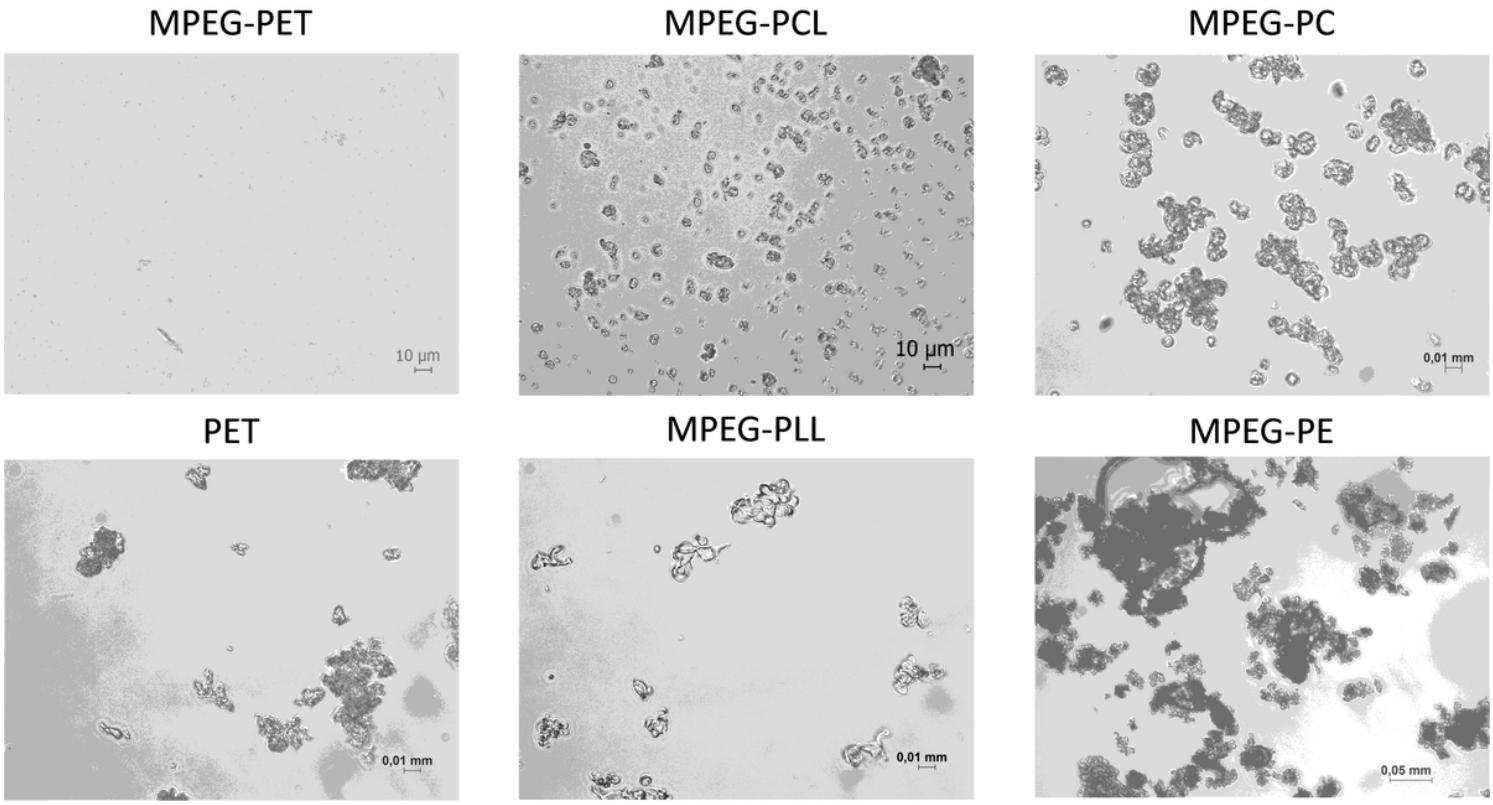

Figure 4

Microscopy images of microparticles redispersed in water. Note the different scale-bar for MPEG-PE

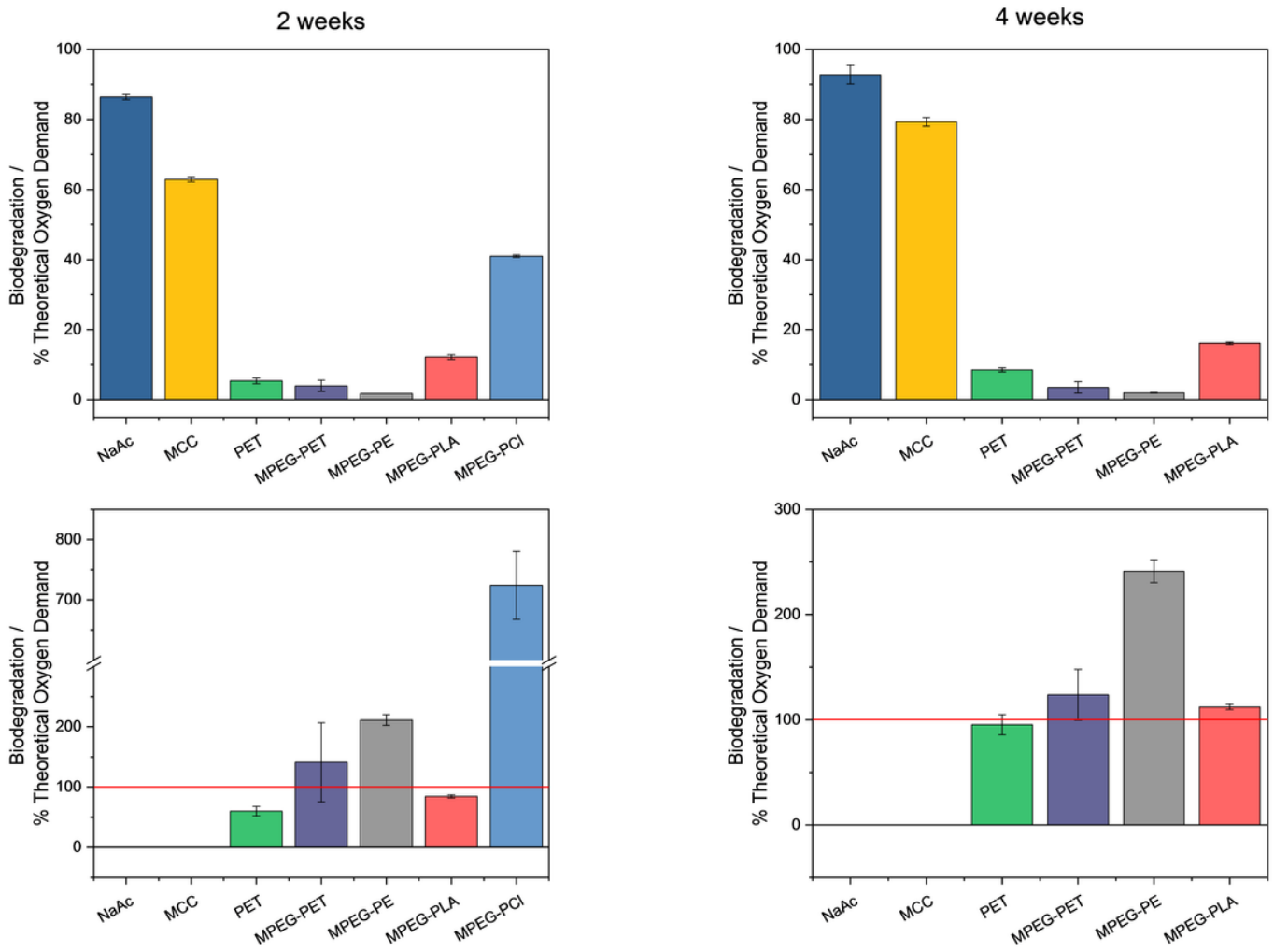

Figure 5

Biodegradation of polymer particles. A: Degradation after 2 and 4 weeks measured versus total theoretical oxygen demand. B: Degradation after 2 and 4 weeks measured versus oxygen demand assuming only MPEG or residual solvent degrades (for MPEG-containing polymers). Controls: NaAc: Sodium Acetate. MCC: Microcrystalline cellulose. The majority of samples were run in duplicate (NaAc, MCC, MPEG-PE, MPEG-PET) with uncertainties given as the difference between the maximum and the minimum values divided by two. For the remaining particles (PET, MPEG-PLA, MPEG-PCL), samples were run in triplicate and the uncertainty is the standard error of the mean. Note that the MPEG-PCL results are shown only for the 2 week series because the BOD capacity of the system was exceeded at subsequent timepoints.

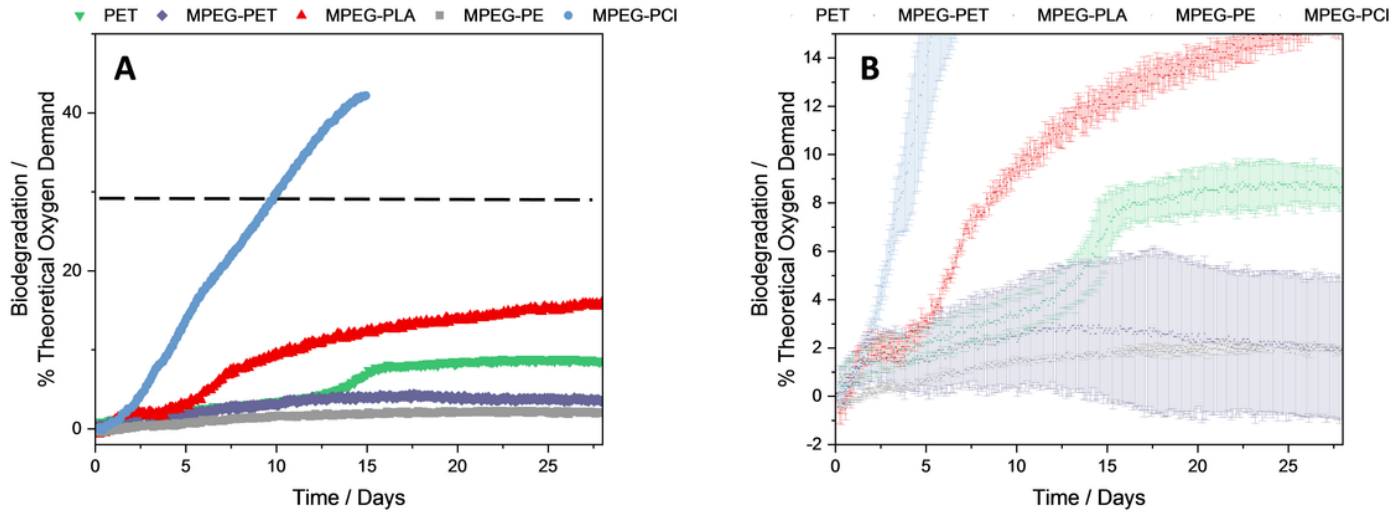

Figure 6

Biodegradation as a function of time A) Degradation of all polymers. The horizontal line indicates 80 mg/L BOD, which is the stated maximum capacity of the system B) Close-up of biodegradation including error bars. Note that the MPEG-PCL results are shown only until 15 days after which the BOD capacity of the test system (80 mg/L) is exceeded. A subsequent test demonstrated a continued degradation of MPEG-PCL beyond the 15 days period (data not shown)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Supportinginformation.docx
- Scheme1.png