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# Degradable and Recyclable Polyesters from Multiple Chain Length Bio- and Waste-Sourceable Monomers

Taylor F. Nelson<sup>†,\*</sup>, Dario Rothauer<sup>†</sup>, Michael Sander, and Stefan Mecking<sup>\*</sup>

**Abstract:** Monomers sourced from waste or biomass are often mixtures of different chain lengths; e.g. catalytic oxidation of polyethylene waste yields mixtures of dicarboxylic acids (DCAs). Yet, polyesters synthesized from such monomer mixtures have rarely been studied. We report polyesters based on multiple linear aliphatic DCAs, present in chain length distributions that vary in their centers and ranges. We demonstrate that these materials can adopt high-density polyethylene-like solid state structures, and are ductile (e.g.  $E_t$  610 MPa), allowing for injection molding, or film and fiber extrusion. Melting and crystallization points of the polyesters show no odd-even effects as dipoles cannot favorably align in the crystal, similar to traditional odd carbon numbered, long-chain DCA polyesters. Biodegradation studies of  $^{13}\text{C}$ -labelled polyesters in soil reveal rapid mineralization, and depolymerization by methanolysis indicates suitability for closed-loop recycling.

highest production volume - is limited in scope as it often results in a deterioration of materials properties.<sup>[3]</sup> Chemical recycling<sup>[4]</sup> is hindered by the inert nature of polyethylene hydrocarbon chains which results in high energy demand for breakdown to ethylene monomer and low efficiencies.<sup>[5]</sup> The lack of functional groups in polyethylene backbones also precludes biodegradability, resulting in accumulation of polyethylene in the environment. Therefore, alternatives to polyethylene are desirable, which have similar properties but (i) are derived from feedstocks other than crude oil,<sup>[6-9]</sup> (ii) are amenable to chemical recycling via incorporated in-chain functional groups,<sup>[4,10,11]</sup> and (iii) in specific applications or as a backstop to other waste management strategies, are biodegradable under environmental conditions.<sup>[12]</sup>

In particular, long-chain aliphatic polyesters have been proposed as sustainable alternatives to high-density polyethylene (HDPE), as their long methylene chains can align to mimic HDPE crystal structures and thus materials properties, while the introduction of ester functional groups into the hydrocarbon backbone enables chemical recycling to monomers via solvolysis of the ester predetermined breaking points.<sup>[11,13]</sup> The required monomers can be constructed from renewable resources: for example, 1,18-octadecanedioate ( $\text{C}_{18}$ ) is accessible via olefin metathesis or biotechnological  $\omega$ -oxidation of oleate-rich feedstocks like high oleic sunflower, soy or palm oil.<sup>[14,15]</sup> In particular, it would be desirable to use lower value monomer sources, which contain distributions of multiple chain lengths, provided that the resulting polymers have properties on par with those from single chain length monomers. A prominent example of such a feedstock is obtained from the oxidation of HDPE, which has been explored already in the early days of polyolefin technology.<sup>[16-18]</sup> More recently, this process has re-emerged to prominence with Co(II)/Mn(II) catalyzed oxidation by air,<sup>[19]</sup> promoted by N-hydroxyphtalimide initiator,<sup>[20]</sup> which has been established as a strategy for the valorization of HDPE waste to dicarboxylic acids (DCAs).<sup>[21-23]</sup> Utilization of the resulting multiple chain length DCAs as microbial feedstocks has been demonstrated for the production of polyhydroxyalkanoates,<sup>[22]</sup> or other high-value chemical compounds.<sup>[23,24]</sup> Additional feedstock streams comprising mixtures of chain lengths include fatty acid methyl esters (FAME) obtained from transesterification of plant and algae oils. Such feedstocks vary in their exact compositions but are typically composed of mixtures of even-carbon numbered long-chain FAMES with varying degrees of unsaturation. FAMES can further be converted to DCAs via olefin metathesis or alkoxy-carbonylation if unsaturation is present.<sup>[25]</sup> Furthermore, metabolic engineer-

## Introduction

Plastics are essential components of practically any current technology and are therefore ubiquitous in everyday life of the modern era. Consequently, plastics are produced on an enormous scale, with petroleum-based thermoplastics dominating the total plastics production volume.<sup>[1]</sup> Thermoplastics' production consumes substantial amounts of crude oil as feedstock, with 6% of this finite resource funneled into plastic production annually.<sup>[2]</sup> At the same time, plastics are largely disposed of after their service life.<sup>[1]</sup> Mechanical recycling of polyethylene - the synthetic polymer with

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ing has been used to biocatalytically produce DCAs from FAME and alkane feedstocks,<sup>[26–29]</sup> or from glucose or glycerol as sole carbon source.<sup>[30]</sup> Resulting DCA mixtures might contain even- or odd-only carbon numbers, depending on the feedstocks used or biocatalytic pathway(s) employed.

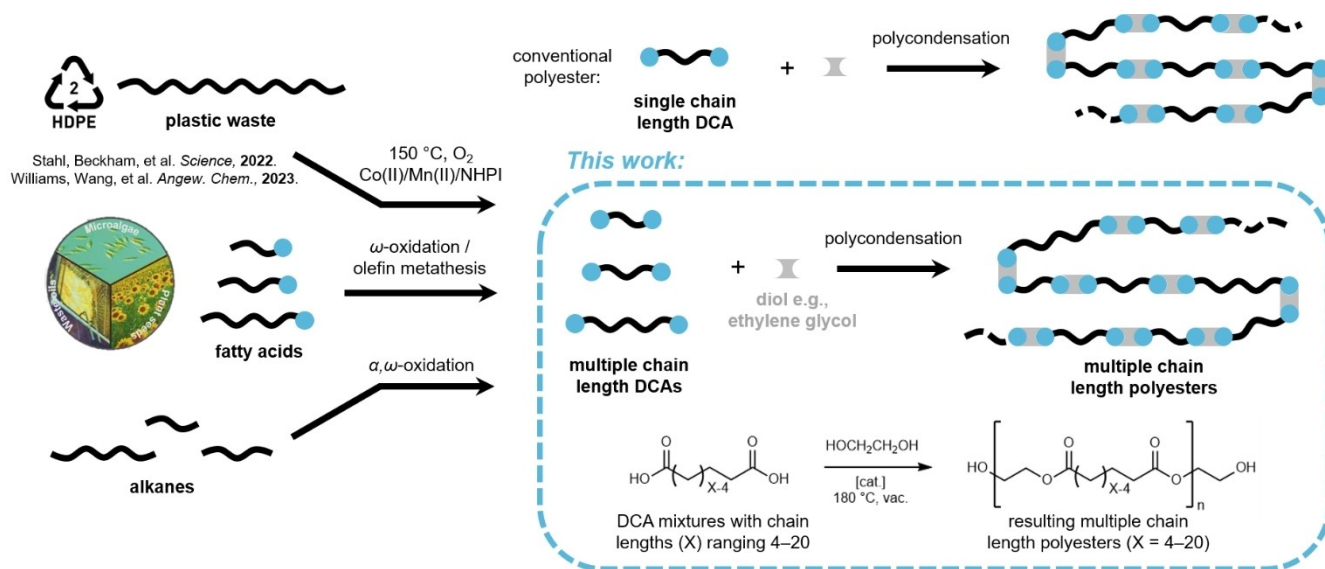
Despite a century of polyester research and development, materials with multiple chain length repeat units as derived from DCA mixtures have rarely been investigated.<sup>[31–33]</sup> We now report the materials properties and biodegradation behavior of polyesters (PE) **PE-2,X±Y**, where 2 refers to the C<sub>2</sub> length of the utilized diol ethylene glycol and *X* refers to the C<sub>*X*</sub> average length of the utilized mixture of dicarboxylates which have multiple different chain lengths that vary from the average by a value of *Y* (Figure 1). We reveal the effect of the distribution center and range of dicarboxylate chain lengths on thermal and structural properties of the resulting polyesters, as compared to the analogous polyesters from a single dicarboxylate monomer (i.e., **PE-2,X**). We show that such polyesters from multiple chain length monomer feedstocks are versatile polymers, presenting opportunities for recyclable, (bio)degradable, and sustainable materials.

## Results and Discussion

### Dicarboxylate Chain Lengths from Chain Scission Processes

To elucidate the nature of DCA chain length distributions expected from a top-down approach, like HDPE oxidation, the random cleavage of polymer chains was modelled. This showed that a broad range of chain lengths is formed, with the short chain products prevailing as soon as the number of cleavage events exceeds ca. 5 per 100 cleavable bonds (for details of a modelled HDPE with *M<sub>n</sub>* of 10 kg mol<sup>-1</sup> ≈ 750

cleavable bonds per chain see the Supporting Information, Figure S1). Note the simulated DCA chain lengths and distributions are also essentially independent of the polymers' starting molecular weight for practical purposes (e.g., for an HDPE with *M<sub>n</sub>* of 100 kg mol<sup>-1</sup>, the same DCA chain length distribution would be obtained). From the viewpoint of chemical reactivity of the hydrocarbon chains the assumption of random cleavage appears reasonable as already formed carboxylic groups will only influence the reactivity of the two adjacent carbons to a relevant extent. From a process-oriented perspective, phase separation of the more polar oxidation products from the polyethylene melt, or different partitioning of the products and the polyethylene starting material as well as the catalyst in solvent systems, respectively, can alter the reactivity in dependence of the cleavage products' chain lengths. This may potentially be beneficial to control product chain length distributions. In any case, mixtures of different chain lengths are expected. Note that the available semi-quantitative experimental data on the distributions of DCAs formed with the aforementioned state-of-the-art oxidation system<sup>[22,23]</sup> agrees with one theoretically obtained when assuming random chain scission. The dimethyl esters, easily obtained from DCAs, are sufficiently volatile to allow for distillation at least up to the C<sub>20</sub> dimethyl ester (boiling point of dimethyl icosanedioate = 223–224 °C at 3 mbar).<sup>[34]</sup> Furthermore, pH-dependent solubilization-based separations can be used to separate groups of long-chain DCAs.<sup>[23]</sup> Thus, a fractionation into different, narrower DCA chain length distributions than obtained directly from HDPE waste oxidation processes and their valorization also appears feasible.



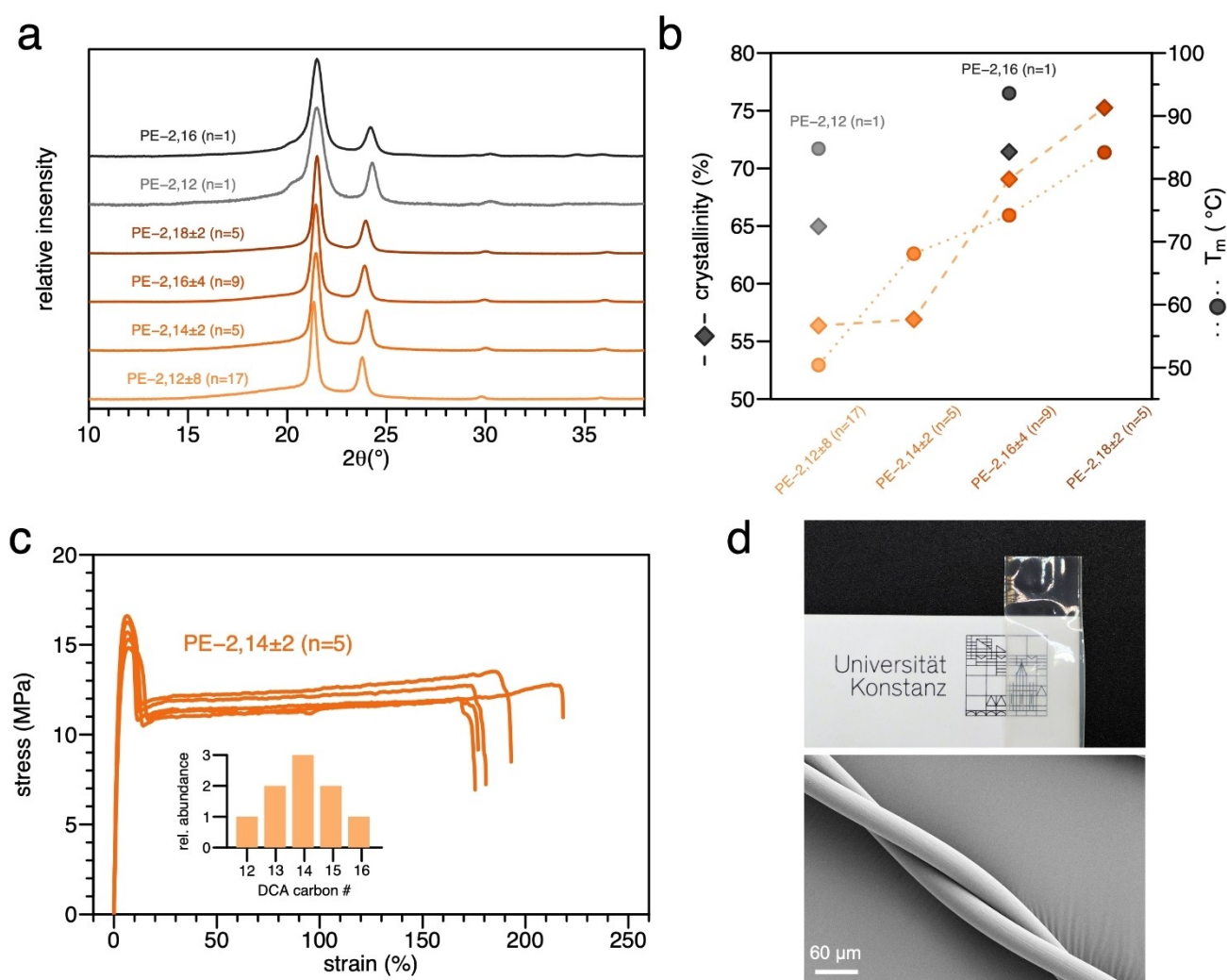
**Figure 1.** Production of multiple chain length dicarboxylate polyesters. Dicarboxylate (DCA) mixtures of multiple chain lengths can be produced directly via oxidation of HDPE waste, or by oxidation of fatty acids from bio-based sources, or alkanes. Polycondensation with ethylene glycol yields polyesters with multiple chain length repeat units.

### Materials properties of Polyesters from Multiple Chain Length Dicarboxylates

To elucidate the role of DCA length distributions on material properties of the resulting polyesters, a variety of different dicarboxylate distributions varying in their center and range of chain lengths were polycondensed with ethylene glycol, yielding polyesters of the form **PE-2,  $X \pm Y$**  ( $n=N$ ), where  $X$  is the length of the center-DCA of each distribution and  $Y$  corresponds to the range of the distribution, composed of  $N$  different DCAs used in the mixture. In each distribution, the center DCA was present with the highest mass, with the mass contributions decreasing for shorter and longer DCAs (see Table S1 of the Supporting Information for details of the nomenclature for the poly-

esters, and Table S2 for the DCA chain length distributions used for each polyester).

Wide angle x-ray scattering (WAXS) analysis of different multiple chain length repeat unit polyesters showed orthorhombic solid-state structures characteristic of HDPE, revealing that the alignment of methylene segments dominates the solid-state also when mixtures of DCAs are present in the polyester backbone, like in traditional single-chain length monomer polyesters,<sup>[35]</sup> exemplified here by **PE-2,12** ( $n=1$ ) and **PE-2,16** ( $n=1$ ) (Figure 2a). Deconvolution of the WAXS diffractograms afforded degrees of crystallinities of 56, 57, 69, and 75 % for **PE-2,12 ± 8** ( $n=17$ ), **PE-2,14 ± 2** ( $n=5$ ), **PE-2,16 ± 4** ( $n=9$ ), and **PE-2,18 ± 2** ( $n=5$ ), as compared to 65 and 71 % for **PE-2,12** ( $n=1$ ) and **PE-2,16** ( $n=1$ ) (for fits of the WAXS diffractograms see Supporting Information Figures S2–7). This trend in crystal-



**Figure 2.** Materials properties of polyesters from dicarboxylate distributions. a: Wide angle x-ray scattering (WAXS) diffractograms. b: Crystallinities (diamonds, left y-axis), as calculated from WAXS diffractograms (a), and melting temperatures ( $T_m$ ; circles, right y-axis) measured from 2<sup>nd</sup> DSC heating cycles at 10 K min<sup>-1</sup>. Points show single determinations with dashed/dotted lines representing linear interpolations to guide the eye. c: Stress-strain curves measured on injection-molded specimens of the polyester **PE-2,14 ± 2** ( $n=5$ ); curves from five replicate samples are shown. Inset shows quantitative relative abundance of different chain length dicarboxylic acids (DCAs) utilized in the polyester. d: Photograph of an exemplary extruded film of **PE-2,14 ± 2** ( $n=5$ ) (top) and scanning electron micrograph of an exemplary melt spun fiber of the same polyester (bottom).

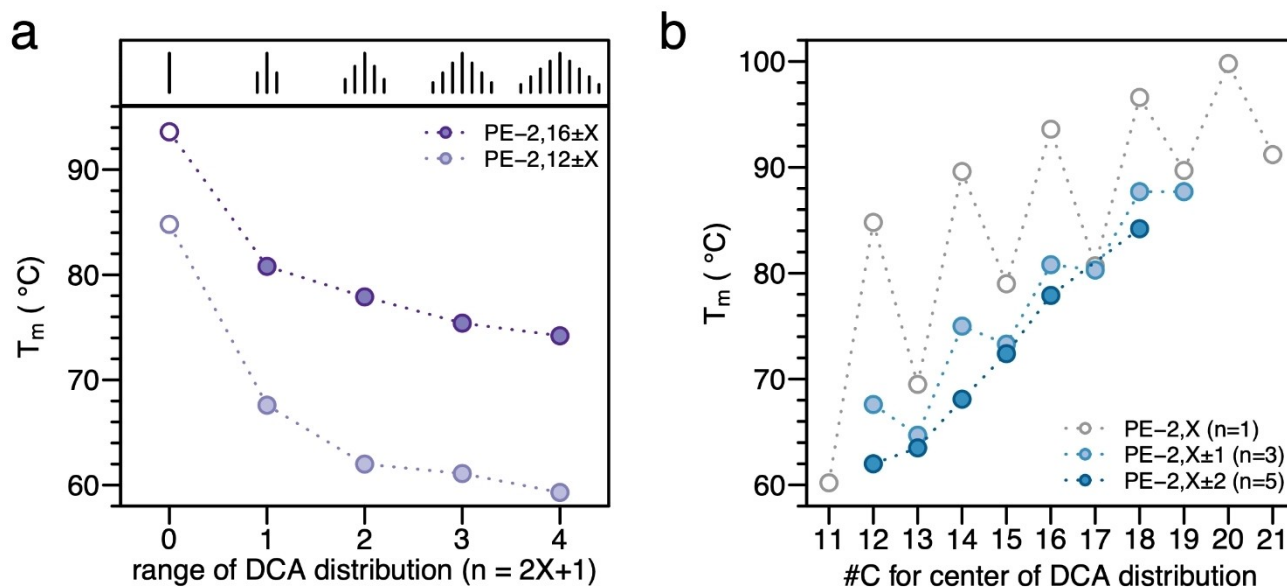
linities was paralleled by an increase in measured  $T_m$  for the same polyesters (Figure 2b). These trends indicate that the solid-state structures of multiple chain length repeat unit polyesters is primarily affected by the center chain length of the included DCA distribution, with longer multiple chain length polyesters exhibiting higher crystallinities regardless of the distribution range. Crystallization observation of reference single chain length polyesters from even carbon number DCAs under cross polarized light microscopy revealed formation of large spherulites (up to approx. 500  $\mu\text{m}$ ) (Figures S8–10). In contrast, representative multiple chain length polyesters (i.e.; **PE-2,16 $\pm$ 2** ( $n=3$ ); **PE-2,18 $\pm$ 2** ( $n=5$ ); and **PE-2,12 $\pm$ 8** ( $n=17$ )) formed small crystallites with a high nucleation density upon the same crystallization process (Figures S11–13). While the formation of spherulites in single chain length polyesters upon crystallization has been observed previously,<sup>[36]</sup> the hindrance of spherulite formation in the multiple chain length polyesters may be related to a lower symmetric nature of the methylene chain sequences.<sup>[36–39]</sup>

To investigate the processability and mechanical properties of polyesters from dicarboxylate distributions, **PE-2,14 $\pm$ 2** ( $n=5$ ) and **PE-2,12 $\pm$ 8** ( $n=17$ ) were prepared in larger batches utilizing dibutyl tin oxide catalyzed polycondensation with a final temperature of 180 °C at <0.1 mbar vacuum for 8 hours. Under these optimized conditions, high molecular weights of up to  $M_n=58 \text{ kg mol}^{-1}$ , as determined by SEC vs. polystyrene standards, could be achieved (for details of polymerization procedures see the Experimental Section in the Supporting Information). Injection-molding of **PE-2,14 $\pm$ 2** ( $n=5$ ) yielded specimens used for stress-strain experiments. The polyester **PE-2,14 $\pm$ 2** ( $n=5$ ) proved

to be a reproducibly ductile material, exhibiting a Young's Modulus ( $E_t$ ) of 610 ( $\pm 30$ ) MPa and stress at yield ( $\sigma_y$ ) of 15.7 ( $\pm 0.7$ ) MPa (average values  $\pm$  s.e. measured on 5 samples; Figure 2c. Literature values<sup>[40]</sup> for HDPE are  $E_t=885$  MPa,  $\sigma_y=27$  MPa and for LDPE  $E_t=240$  MPa,  $\sigma_y=12$  MPa). Meanwhile, injection molding of the wider DCA distribution polyester **PE-2,12 $\pm$ 8** ( $n=17$ ) expectedly yielded softer material ( $E_t=170$  ( $\pm 10$ ) MPa;  $\sigma_{\text{max}}=5.7$  ( $\pm 0.1$ ) MPa; see Supporting Information Figure S14;  $M_n=39 \text{ kg mol}^{-1}$  according to SEC vs. PS standards) that displayed a brittle behaviour. Higher molecular weight polyesters from these extremely broad DCA distributions may be required to improve mechanical properties. The **PE-2,14 $\pm$ 2** ( $n=5$ ) polymer melt was also processable into thin films (thickness of 27 ( $\pm 2$ )  $\mu\text{m}$ ) via extrusion, and into fibers (a strand of 400 m with diameter of 33.8 ( $\pm 0.4$ )  $\mu\text{m}$ ) via extrusion melt spinning (Figure 2d; see Supporting Information Figure S15 for a photograph of the fiber roll).

To map the role of dicarboxylate distribution on thermal properties, a large variety of different **PE-2,X $\pm$ Y** ( $n=N$ ) were prepared in small-scale polycondensation experiments and analyzed using differential scanning calorimetry (DSC; see Supporting Information Figures S16–22 for DSC heating/cooling traces and Table S2 for a list of the results, see Supporting Information Figures S23–38 for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of selected polyesters). The melting temperatures ( $T_m$ ) of some series of selected polyesters are shown in Figure 3.

Polyesters synthesized from multiple chain length DCAs resulted in lower  $T_m$  as compared to analogous polyesters from a single chain length DCA (Figure 3a). This was observed for both  $\text{C}_{12}$ - and  $\text{C}_{16}$ -centered distributions from



**Figure 3.** Thermal properties of selected polyesters from different distributions of long-chain dicarboxylates (DCAs). a: Polyester melting temperature ( $T_m$ ) vs. DCA distribution range ( $X$ ), either for  $\text{C}_{12}$ -DCA (light purple) or  $\text{C}_{16}$ -DCA (dark purple) centered distributions. Relative masses of each DCA employed per polymer are represented above the plot. b: polyester  $T_m$  vs. the number-center of different DCA distributions, each for distributions from a single DCA (grey, open symbols), three DCAs (i.e., center  $\pm 1$ ; light blue), or five DCAs (i.e., center  $\pm 2$ ; dark blue). Points show single measurements with dotted lines as linear interpolations to guide the eye. Select  $T_m$  values are also reported in Figure 2b.

three DCAs each (i.e. ( $X \pm 1$ ,  $n=3$ ), with  $T_m$  68 vs. 85 ( $X=12$ ) and 81 vs. 94 °C ( $X=16$ ), respectively. Further decreases of  $T_m$  to 59 and 74 °C were found when increasing the distribution range to ( $X \pm 4$ ,  $n=9$ ) DCAs, corresponding to ranges of DCAs from  $C_8$ – $C_{16}$  and  $C_{12}$ – $C_{20}$ . In addition, the polyester from  $C_4$ – $C_{20}$  DCA (**PE-2,12 $\pm$ 8** ( $n=17$ )), corresponding to the wide range of DCAs that can be formed in Co(II)/Mn(II) co-catalyzed oxidation of HDPE,<sup>[22,23]</sup> was synthesized and showed a  $T_m$  of 50 °C.

Increasing the center of the DCA distribution generally increased the  $T_m$  of the resulting polyesters, for both single and multiple chain length DCA distributions (Figure 3b). Conventional polyesters from singular even-carbon number DCAs (in combination with an even carbon number diol) show higher  $T_m$  compared to the odd-carbon number analogues. This “odd-even” effect is well documented, and arises from the favorable dipole alignment of adjacent chain segments in the crystallites for even-carbon numbered polyesters, which is lacking in the odd-carbon numbered analogues.<sup>[35,36,39,41]</sup> Notably, when a mixture of DCAs is incorporated into the polyesters, the “odd-even” effect on  $T_m$  was no longer present, with generally continuous increases in  $T_m$  observed for PE-2, $X \pm 1$  and PE-2, $X \pm 2$  polyesters, regardless of whether the center of the DCA distribution is even- or odd-carbon numbered, and the melting points approached those of reference odd carbon number polyesters PE-2, $X$ .

#### Deconstruction of Polyesters from Dicarboxylate Distributions

In a preliminary chemical recycling experiment, **PE-2,14 $\pm$ 2** ( $n=5$ ) was subjected to methanolysis at 150 °C for 4 days. A mixture of  $C_{12}$ – $C_{16}$  dimethyl esters (DMEs) could be recovered quantitatively after solvent removal *in vacuo*. The ratio of DCAs employed in the polyesters’ synthesis was maintained (i.e., 1:2:3:2:1 by weight for  $C_{12}$ : $C_{13}$ : $C_{14}$ : $C_{15}$ : $C_{16}$ ) as evidenced by GC-FID and ESI-MS analysis of the resulting DME mixture; that is no DCAs were lost, suggesting the recovered monomer mixture is suitable for generating identical composition polyester again (see Supporting Information Figures S39–44). Methanolysis has been demonstrated as a strategy for chemical recycling of semi-crystalline aliphatic polyesters (e.g., PE-18,18<sup>[11]</sup> and PE-2,18<sup>[13]</sup>), yielding high recoveries of the monomers with high purities and enabling re-polymerization of the polyesters with similar properties to those of the virgin materials. The obtained results indicated that this strategy can be adapted to further HDPE-like polyesters, including those which are composed of DCA monomers with differing lengths.

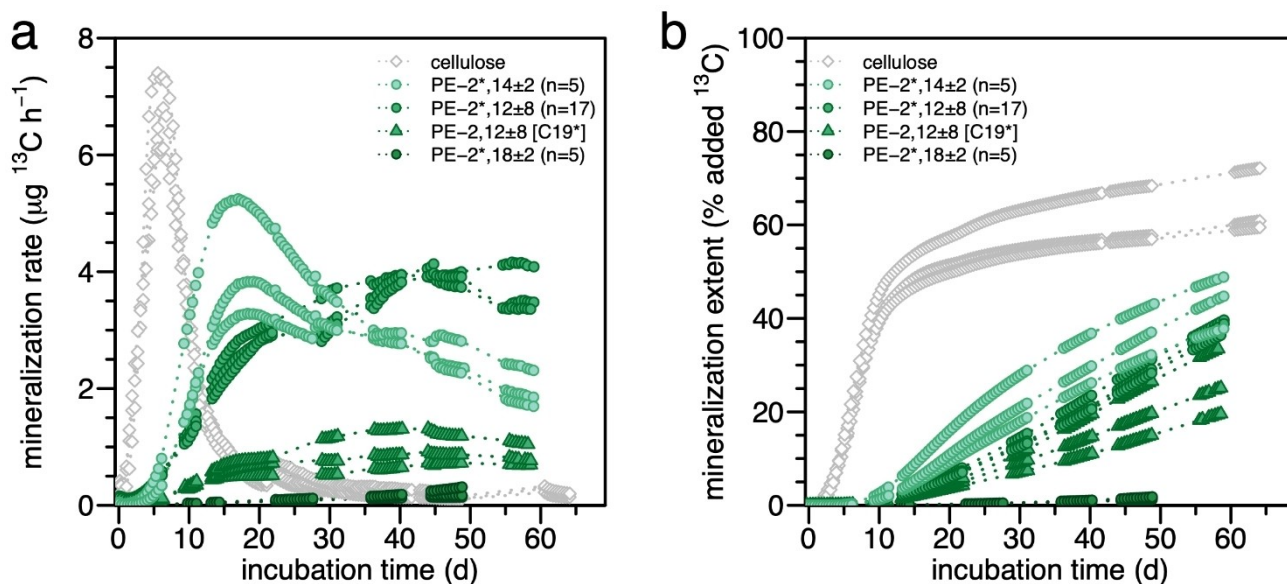
To investigate the biodegradability of the polyesters, <sup>13</sup>C-labelled variants of select **PE-2, $X \pm Y$**  were incubated in an agricultural soil, with isotope-selective (<sup>13</sup>C & <sup>12</sup>C) quantification of the soil efflux CO<sub>2</sub>. At the same time, controls containing <sup>13</sup>C-labelled cellulose as a positive control for biodegradation were incubated using the same soil. The measurement system used has been previously established to quantitatively follow the mineralization of <sup>13</sup>C-labelled

biodegradable polyesters in soil.<sup>[42,43]</sup> Here, the mineralization rates and extents of **PE-2,12 $\pm$ 8** ( $n=17$ ); **PE-2,14 $\pm$ 2** ( $n=5$ ); and **PE-2,18 $\pm$ 2** ( $n=5$ ), along with those of cellulose, were followed over the course of two months (Figure 4). Each of the three polyesters were synthesized using <sup>13</sup>C<sub>2</sub>-ethylene glycol (EG), meaning the <sup>13</sup>C-label (indicated below by \*) was in the ethylene glycol monomer unit; an additional variant of **PE-2,12 $\pm$ 8** ( $n=17$ ) instead contained the <sup>13</sup>C-label throughout the nonadecanedioate ( $C_{19}$ -DCA) monomer unit (i.e., **PE-2,12 $\pm$ 8** ( $n=17$ ) [ $C_{19}$ \*]).

The polyesters **PE-2,14 $\pm$ 2** ( $n=5$ ) and **PE-2,12 $\pm$ 8** ( $n=17$ ) showed an exponential increase in their <sup>13</sup>C-mineralization rates for the first two weeks after their addition to soil. After this time, the <sup>13</sup>C-mineralization rates of **PE-2\*,14 $\pm$ 2** began to slowly decrease, while those for both forms of **PE-2,12 $\pm$ 8** ( $n=17$ ) slightly increased and remained relatively constant for the remainder of the incubation period. After two months, the polyesters **PE-2\*,14 $\pm$ 2** ( $n=5$ ); **PE-2\*,12 $\pm$ 8** ( $n=17$ ); and **PE-2,12 $\pm$ 8** ( $n=17$ ) [ $C_{19}$ \*] showed <sup>13</sup>C-mineralization extents of 44 ( $\pm 6$ )%, 38 ( $\pm 2$ )%, and 26 ( $\pm 7$ )%, respectively, expressed as a percent of the added <sup>13</sup>C. Lower net <sup>13</sup>C-mineralization rates of **PE-2,12 $\pm$ 8** ( $n=17$ ) [ $C_{19}$ \*] than **PE-2\*,12 $\pm$ 8** ( $n=17$ ) were in part due to the fact that less amounts of <sup>13</sup>C were present in the former polyester. When normalized to the amount of polyester-<sup>13</sup>C added, the extent of mineralization for **PE-2\*,12 $\pm$ 8** ( $n=17$ ) was still higher than that of **PE-2,12 $\pm$ 8** ( $n=17$ ) [ $C_{19}$ \*]. The overall mineralization rate is a result of the two consecutive steps in polyester biodegradation: (i) polyester hydrolysis catalyzed by extracellular esterases, and (ii) microbial uptake and utilization of the resulting hydrolysis products, either to produce energy with CO<sub>2</sub> as a byproduct or to assimilate into microbial biomass. As the hydrolysis rate should not differ for the sample polymer containing <sup>13</sup>C in the EG or  $C_{19}$ -DCA monomer units, the difference in mineralization extents suggests that the EG monomer unit carbon is faster or more extensively mineralized than that of the  $C_{19}$ -DCA monomer unit. This could mean that uptake and utilization of  $C_{19}$ -DCA is slower than of EG by microbes, or that carbon from  $C_{19}$ -DCA is more preferentially assimilated into microbial biomass (vs. mineralized) as compared to EG-carbon.

At the same time, **PE-2\*,18 $\pm$ 2** ( $n=5$ ) showed a slow, continual increase in its <sup>13</sup>C-mineralization rate (see Supporting Information Figure S45 for more detailed mineralization curves of **PE-2\*,18 $\pm$ 2** ( $n=5$ )). Nonetheless, the rates remained  $< 0.5 \mu\text{g}^{13}\text{C h}^{-1}$ , meaning that after 50 days of incubation, the <sup>13</sup>C-mineralization extent reached 1.5 ( $\pm 0.3$ ) % of the added <sup>13</sup>C. The markedly slower mineralization of **PE-2\*,18 $\pm$ 2** ( $n=5$ ) compared to the other polyesters may be related to its higher  $T_m$  (84 °C vs. 68 °C & 50 °C; Figure 2b) or its higher crystallinity (75 % vs. 57 % & 56 %; Figure 2b), which both are indicators of a more limited flexibility of the polymer chains, and therefore reduce accessibility of the ester bonds for extracellular esterases.<sup>[44]</sup>

These results demonstrate the potential for polyesters derived from mixtures of long-chain DCAs to biodegrade in natural environments. In particular, those with relatively lower center-DCAs (e.g., **PE-2,14 $\pm$ 2** ( $n=5$ )), and/or broad-



**Figure 4.** Soil biodegradation of selected  $^{13}\text{C}$ -labelled polyesters from different distributions of long-chain dicarboxylates (DCAs).  $^{13}\text{C}$ -labelling was achieved by employing  $^{13}\text{C}_2$ -ethylene glycol (PE-2\*,14±2 (n=5); PE-2\*,12±8 (n=17); and PE-2\*,18±2 (n=5) or  $^{13}\text{C}_{19}$ -nonadecanedioic acid (PE-2\*,12±8 (n=17) [C $_{19}^*$ ]).  $^{13}\text{C}$ -labelled cellulose was added to control bottles as a reference biodegradable polymer in the same soil. Polymers were added as particles to an agricultural soil, and mineralization rates were calculated from isotope-selective quantification of the soil efflux  $\text{CO}_2$ . Points show measured values for individual incubation bottles, with dotted lines showing linear interpolations to guide the eye. Longer gaps between measurement points indicate times when the samples were detached from the incubation system, to allow measurement of different samples. Mineralization rates of  $^{13}\text{C}$  (a) were integrated over time to yield  $^{13}\text{C}$ -mineralization extents, which were normalized to the amount of polyester-derived  $^{13}\text{C}$  added to the soils (b).

er DCA distributions (e.g., PE-2,12±8 (n=17)) showed significant mineralization in an agricultural soil after a few months of incubation time, especially when compared relative to cellulose mineralization measured within the same time. Within two months in the studied soil, cellulose reached a  $^{13}\text{C}$ -mineralization extent of 64 (±7)% of the added  $^{13}\text{C}$ , displaying two distinct mineralization phases, as has been demonstrated previously:<sup>[42]</sup> The first phase (approx. 0–15 days after addition to soil) was characterized by a fast rate, corresponding to direct mineralization of cellulose carbon during microbial utilization. During this time, cellulose carbon was also assimilated into microbial biomass, the extent of which is defined by the carbon use efficiency (CUE; i.e., ratio of mineralized carbon to the total amount of utilized carbon). The second phase (>15 days after addition to soil) was characterized by a slower mineralization rate, likely corresponding to turnover of the cellulose carbon which was microbially assimilated during the first phase, into  $\text{CO}_2$ . In contrast, the polyesters appeared to mineralize with more constant rates, indicating that the depolymerization of the polyesters to bioavailable units was slower than that of cellulose.

## Conclusion

Our findings demonstrate the viability of semi-crystalline polyester materials from dicarboxylates (DCAs) of multiple chain lengths, which can be generated from the oxidation of polyethylene waste, or potentially from biological feed-

stocks. Despite the highly irregular spacing of ester groups in the polyester chains, they were able to crystallize to orthorhombic crystal structures similar to those formed in polyethylene and long-chain HDPE-like polyesters from single repeat unit length monomers.<sup>[13,36,39]</sup> As expected, melting and crystallization transitions of multiple chain length polyesters occur at lower temperatures than for traditional single repeat unit type polyesters. As the distribution of DCAs broadens, odd-even effects on these thermal properties become irrelevant, and melting temperatures of multiple chain length polyesters approach those of single (odd)-repeat unit analogues, both for even- and odd-carbon number centers of the distributions. Crystallization temperatures that allow for thermoplastic processing could be achieved with e.g. a  $\text{C}_{12}$  to  $\text{C}_{16}$  distribution (i.e.,  $T_m = 68^\circ\text{C}$ ;  $T_c = 46^\circ\text{C}$ ). Softer polyesters from very broad distributions, and resultant lower  $T_m$  and  $T_c$  (e.g., a  $\text{C}_4$  to  $\text{C}_{20}$  distribution), may serve as crystalline adhesives. Further, the solvolytic recycling process previously demonstrated<sup>[11]</sup> is feasible without losses that would have altered monomer composition, beneficial for possible closed-loop recycling approaches. The results provide guidelines for the further development of these materials and for recycling process.

Notably, these materials possess favorable degradability. While the long-chain aliphatic PE-2,18 has been shown to mineralize rapidly under industrial composting conditions,<sup>[13]</sup> we now report biodegradation of multiple chain length analogues by native soil microorganisms under more environmentally relevant conditions. The polyesters from relatively lower center-DCAs (e.g., PE-2,14±2 (n=5)), and/or

broader DCA distributions (e.g., **PE-2,12±8 (n=17)**) showed significant mineralization within two months, with even the higher-center DCA polyester **PE-2,18±2 (n=5)** expressing a non-zero mineralization rate, indicating that such longer-chain polyesters also have the potential to be slow-biodegrading in the natural environment. These observed differences in mineralization rates suggest that biodegradation rates in the environment of aliphatic polyesters might be tunable by adjusting the center and range of dicarboxylate monomer unit chain lengths. Future investigations on the degradation of such polyesters should further elucidate the interplay between monomer distributions, polymer properties and their degradability, and would be required to assess their long-term fate in the environment. Additional characterization of non-mineralized polyesters such as their extraction from soil,<sup>[45]</sup> or analysis of their assimilation into microbial biomass,<sup>[43]</sup> could further inform about the ultimate fate of these materials.

Although some reports of HDPE oxidation in air suggest DCAs are formed exclusively, the formation of other products like ketones, secondary alcohols, and monocarboxylates must also be considered.<sup>[46–49]</sup> Further elucidation of the oxidation selectivity and process improvements appear warranted, as does the potential utilization of multiple chain length DCA feedstocks that contain additional functional groups such as ketones. In summary, the approach presented allows for the generation of sustainable polyester materials from multiple chain length DCAs like those accessible from HDPE waste, an abundantly available feedstock for the foreseeable future.

### Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[50–52]</sup>

### Author Contributions

T.F.N., D.R., and S.M. jointly devised the experimental program; T.F.N. and D.R. conducted polymerization experiments and characterizations; T.F.N. and M.S. conducted biodegradation experiments. All authors contributed to writing the manuscript.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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- [1] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.
- [2] World Economic Forum, Ellen MacArthur Foundation, McKinsey and Company, *The New Plastics Economy: Rethinking the Future of Plastics*, **2016**.
- [3] K. Ragaert, L. Delva, K. Van Geem, *Waste Manage.* **2017**, *69*, 24–58.
- [4] I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2020**, *59*, 15402–15423.
- [5] G. W. Coates, Y. D. Y. L. Getzler, *Nat. Rev. Mater.* **2020**, *5*, 501–516.
- [6] Y. Zhu, C. Romain, C. K. Williams, *Nature* **2016**, *540*, 354–362.
- [7] G. X. De Hoe, M. T. Zumstein, B. J. Tiegs, J. P. Brutman, K. McNeill, M. Sander, G. W. Coates, M. A. Hillmyer, *J. Am. Chem. Soc.* **2018**, *140*, 963–973.
- [8] X. Zhang, M. Fevre, G. O. Jones, R. M. Waymouth, *Chem. Rev.* **2018**, *118*, 839–885.
- [9] R. M. Cywar, N. A. Rorrer, C. B. Hoyt, G. T. Beckham, E. Y.-X. Chen, *Nat. Rev. Mater.* **2022**, *7*, 83–103.
- [10] G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, *Renewable Sustainable Energy Rev.* **2017**, *73*, 346–368.
- [11] M. Häußler, M. Eck, D. Rothauer, S. Mecking, *Nature* **2021**, *590*, 423–427.
- [12] A. C. Albertsson, M. Hakkarainen, *Science* **2017**, *358*, 872–873.
- [13] M. Eck, S. T. Schwab, T. F. Nelson, K. Wurst, S. Iberl, D. Schleheck, C. Link, G. Battagliarin, S. Mecking, *Angew. Chem. Int. Ed.* **2023**, *62*, e202213438.
- [14] S. Huf, S. Krügener, T. Hirth, S. Rupp, S. Zibek, *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 548–561.
- [15] S. Chikkali, S. Mecking, *Angew. Chem. Int. Ed.* **2012**, *51*, 5802–5808.
- [16] A. Keller, Y. Udagawa, *J. Polym. Sci. A-2 Polym. Phys.* **1970**, *8*, 19–34.
- [17] L. R. Melby, *Macromolecules* **1978**, *11*, 50–56.
- [18] H. Alter, *Ind. Eng. Chem.* **1960**, *52*, 121–124.
- [19] R. A. F. Tomás, J. C. M. Bordado, J. F. P. Gomes, *Chem. Rev.* **2013**, *113*, 7421–7469.



- [20] Y. Ishii, S. Sakaguchi, *Catal. Today* **2006**, *117*, 105–113.
- [21] M. W. Guzik, T. Nitkiewicz, M. Wojnarowska, M. Sołtysik, S. T. Kenny, R. P. Babu, M. Best, K. E. O'Connor, *Waste Manage.* **2021**, *135*, 60–69.
- [22] K. P. Sullivan, A. Z. Werner, K. J. Ramirez, L. D. Ellis, J. R. Bussard, B. A. Black, D. G. Brandner, F. Bratti, B. L. Buss, X. Dong, S. J. Haugen, M. A. Ingraham, M. O. Konev, W. E. Michener, J. Miscall, I. Pardo, S. P. Woodworth, A. M. Guss, Y. Román-Leshkov, S. S. Stahl, G. T. Beckham, *Science* **2022**, *378*, 207–211.
- [23] C. Rabot, Y. Chen, S. Bijlani, Y. Chiang, C. E. Oakley, B. R. Oakley, T. J. Williams, C. C. C. Wang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214609.
- [24] E. Bäckström, K. Odellius, M. Hakkarainen, *ACS Sustainable Chem. Eng.* **2019**, *7*, 11004–11013.
- [25] S. Mecking, *Philos. Trans. R. Soc. A* **2020**, *378*, 20190266.
- [26] S. Picataggio, T. Rohrer, K. Deanda, D. Lanning, R. Reynolds, J. Mielenz, L. D. Eirich, *Nat. Biotechnol.* **1992**, *10*, 894–898.
- [27] D. L. Craft, K. M. Madduri, M. Eshoo, C. R. Wilson, *Appl. Environ. Microbiol.* **2003**, *69*, 5983–5991.
- [28] J.-W. Song, E.-Y. Jeon, D.-H. Song, H.-Y. Jang, U. T. Bornscheuer, D.-K. Oh, J.-B. Park, *Angew. Chem. Int. Ed.* **2013**, *52*, 2534–2537.
- [29] F. Wang, J. Zhao, Q. Li, J. Yang, R. Li, J. Min, X. Yu, G.-W. Zheng, H.-L. Yu, C. Zhai, C. G. Acevedo-Rocha, L. Ma, A. Li, *Nat. Commun.* **2020**, *11*, 5035.
- [30] T. U. Chae, J. H. Ahn, Y.-S. Ko, J. W. Kim, J. A. Lee, E. H. Lee, S. Y. Lee, *Metab. Eng.* **2020**, *58*, 2–16.
- [31] P. A. Fokou, M. A. R. Meier, *J. Am. Chem. Soc.* **2009**, *131*, 1664–1665.
- [32] K. Pinsuwan, P. Opaprakasit, A. Petchsuk, L. Dubas, M. Opaprakasit, *Polym. Degrad. Stab.* **2023**, *210*, 110306.
- [33] P. Roesle, F. Stempfle, S. K. Hess, J. Zimmerer, C. Río Bártulos, B. Lepetit, A. Eckert, P. G. Kroth, S. Mecking, *Angew. Chem. Int. Ed.* **2014**, *53*, 6800–6804.
- [34] P. Chuit, J. Hausser, *Helv. Chim. Acta* **1929**, *12*, 850–859.
- [35] F. Stempfle, P. Ortman, S. Mecking, *Chem. Rev.* **2016**, *116*, 4597–4641.
- [36] C. Zhou, Z. Wei, Y. Yu, S. Shao, X. Leng, Y. Wang, Y. Li, *Mater. Today Commun.* **2019**, *19*, 450–458.
- [37] F. Tao, S. L. Bernasek, *Chem. Rev.* **2007**, *107*, 1408–1453.
- [38] R. A. Pérez-Camargo, L. Meabe, G. Liu, H. Sardon, Y. Zhao, D. Wang, A. J. Müller, *Macromolecules* **2021**, *54*, 259–271.
- [39] L. Zhou, P. Qin, L. Wu, B.-G. Li, P. Dubois, *ACS Sustainable Chem. Eng.* **2021**, *9*, 17362–17370.
- [40] D. Jeremic, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, **2014**.
- [41] M. G. Menges, J. Penelle, C. Le Fevere de Ten Hove, A. M. Jonas, K. Schmidt-Rohr, *Macromolecules* **2007**, *40*, 8714–8725.
- [42] T. F. Nelson, R. Baumgartner, M. Jaggi, S. M. Bernasconi, G. Battagliarin, C. Sinkel, A. Künkel, H.-P. E. Kohler, K. McNeill, M. Sander, *Nat. Commun.* **2022**, *13*, 5691.
- [43] M. T. Zumstein, A. Schintlmeister, T. F. Nelson, R. Baumgartner, D. Wobken, M. Wagner, H.-P. E. Kohler, K. McNeill, M. Sander, *Sci. Adv.* **2018**, *4*, eaas9024.
- [44] E. Marten, R. J. Müller, W. D. Deckwer, *Polym. Degrad. Stab.* **2003**, *80*, 485–501.
- [45] T. F. Nelson, S. C. Remke, H. P. E. Kohler, K. McNeill, M. Sander, *Environ. Sci. Technol.* **2020**, *54*, 266–275.
- [46] F. Gugumus, *Polym. Degrad. Stab.* **1990**, *27*, 19–34.
- [47] L. Costa, M. P. Luda, L. Trossarelli, *Polym. Degrad. Stab.* **1997**, *58*, 41–54.
- [48] L. M. Smith, H. M. Aitken, M. L. Coote, *Acc. Chem. Res.* **2018**, *51*, 2006–2013.
- [49] Y. Ahn, G. Roma, X. Colin, *Macromolecules* **2022**, *55*, 8676–8684.
- [50] F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, *Macromolecules* **2011**, *44*, 4159–4166.
- [51] International Organization for Standardization, **2012**.
- [52] International Organization for Standardization, **2018**.

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