

Polyethylene-like materials from plant oils

Stefan Mecking

Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, Germany

Keywords: catalysis, renewable feedstocks, polymer materials, microalgae, degradability, non-persistent plastics

Summary

Polyethylene is the most important synthetic polymer material produced. Its excellent material properties arise from crystalline interactions in its hydrocarbon chains. This simple concept inspires studies of materials based on alternative non-fossil feedstocks and with additional traits such as a non-persistent nature.

Renewable seed oil or microalgae oil lipids can serve as a feedstock for long-chain difunctional monomers. Catalytic conversion of their unsaturated fatty acids by e.g. isomerizing carbonylation or olefin metathesis yields long-chain monomers $X-(CH_2)_n-X$ with 18 to 26 carbon atoms and terminal dicarboxy, diol or diamine groups (X), and ultralong chain polyethylene telechelics with 48 carbon atoms. These can be polymerized to polyesters, polycarbonates and other (ultra)long-chain polycondensates. These in many cases possess polyethylene-like solid state structure and mechanical properties. Unlike polyethylene, they contain in-chain functional groups that can potentially enhance degradability. The crystalline and hydrophobic nature of the polymers decelerates degradation strongly compared to rapidly degrading shorter chain analogs. Our preliminary findings suggest that a non-persistent nature can be achieved for these materials. This review article is based on a lecture held at the Royal Society Discussion Meeting on Science to Enable the Circular Economy.

Main Text

1 Background

Polymer materials, commonly termed ‘plastics’, are ubiquitous and indispensable in modern life. Cell phones, cycling helmets, electrical appliances of any sorts, light-weight and safe vehicles, footwear and sports gear or food containers and packaging are a few examples of myriad applications. Of the different classes of polymers, polyethylene (PE) is the largest in terms of produced volume. More than 100 million tons of polyethylenes are produced every year worldwide. Many different grades of polyethylene exist to fulfil different demands, these are summarized in the classifications HDPE (high density polyethylenes), LDPE (low density polyethylene) and LLDPE (linear low density), to name the most prominent ones. A common feature of all these polyethylenes is crystalline order that arises from non-covalent interactions (van der Waals interactions) between adjacent stretched segments of hydrocarbon chains (Figure 1).^[1] This is particularly pronounced for HDPE, as it is composed of linear chains devoid of branches that would disturb this crystalline packing. This reflects in the mechanical strength of HDPE. Their hydrocarbon nature also makes polyethylenes hydrophobic and apolar. That is, they will not take up water or easily adhere to polar materials like metals or wood. Moreover, due to the chemically inert nature of the hydrocarbon chains, polyethylenes are not susceptible to degradation reactions. This renders them persistent when released to the environment.

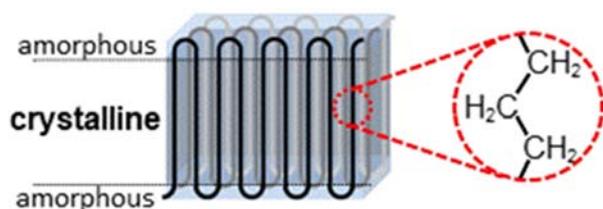


Figure 1. Schematic representation of a folded chain crystallite of polyethylene.

*Author for correspondence (stefan.mecking@uni-konstanz.de).

Polyethylenes are produced by chain growth polymerizations of ethylene, for the most part by catalytic methods (Figure 2, top). The catalysts employed are extremely efficient. However, they are very sensitive to any polar non-hydrocarbon molecules in the feed. This hinders an introduction of functional groups into the polyethylene chains, even in small amounts. The ethylene feedstock is sourced from crude oil, by the process of steamcracking. Crude oil is not only a finite resource on the long term, its recovery and transport is evidently associated with a certain environmental and political risk. Notwithstanding, even in optimistic scenarios the consumption of crude oil is predicted to increase in the foreseeable future. This is due to an offset of savings in power generation and passenger cars by other sectors, the chemical industry and polymer production being a major driver.^[2]

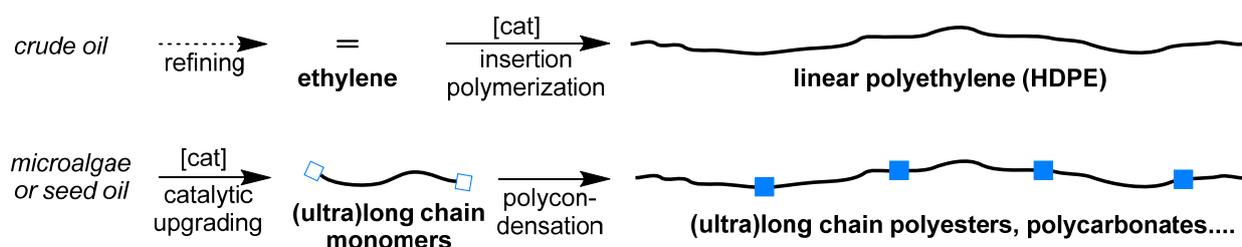


Figure 2. Schematic representation of traditional polyethylene production (top), and generation of (ultra)long-chain polycondensates from plant oils (bottom). The latter polymers possess a hydrocarbon chain $(\text{CH}_2)_n$ akin to polyethylene, but with functional groups (■, e.g. ester, carbonate or acetal groups) in the chain.

The desirable materials properties of polyethylenes on the one hand, and limitations on the other hand motivate an exploration of plant oil-based ‘polyethylene-like’ materials.

2 Monomers

The fatty acid molecules in plant oils are composed of long linear methylene sequences. In order to link them to polymer chains, appropriate reactive groups are required (Figure 2, bottom). A carboxylic acid group is naturally present in fatty acid molecules, as a terminus of the methylene chain. The required second group can be generated by making use of the double bond of unsaturated fatty acids. As this is in the center of the fatty acid molecule, the functional group will usually be generated here. This is the case in traditional methods, which are used to produce sebacic acid (C_{10}) or 11-aminoundecanoic acid (C_{11}) monomers from castor oil.^[3] However, the other half of the fatty acid molecule is essentially lost as waste (Figure 3, (a)). The nylon polymers generated from the aforementioned ‘mid-chain’ monomers do not possess ‘polyethylene-like’ properties, but are rather dominated by the in-chain functional groups. Advanced catalytic methods can provide monomers with the same length as a fatty acid molecule. Olefin metathesis results in a net scrambling of the substituents about a double bond (e.g. $2 \text{R-CH=CH-R} \leftrightarrow \text{R-CH=CH-R} + \text{‘R-CH=CH-R’}$). This occurs to a significant extent in a recently introduced industrial process for the refining of palm oil, yielding the C_{18} linear diacid^[4] after catalytic hydrogenation. A stoichiometric amount of non-functionalized hydrocarbon is formed (Figure 3, (b)), which may be utilized as jet fuel. This can be overcome by using a fundamentally different approach, namely an isomerizing functionalization.^[5] The underlying principle is a dynamic isomerization of the double bond along all positions of the entire fatty acid chain, but with a generation of the desired functional group selectively only at the terminal position opposite to the carboxylic acid group already provided by the fatty acid itself.^[6] By this remarkable reaction, the functional group is generated in a remote position relative to the original position of the double bond, e.g. eight carbon atoms apart. In this way, by an isomerizing alkoxycarbonylation of for example high oleic sunflower oil or erucic acid, respectively, the linear C_{19} or C_{23} diester are formed in high purity.^[7,8] Unlike olefin metathesis, the entire unsaturated fatty acid feedstock is converted to the desired monomers, and the full length of the fatty acid methylene chain is found in the monomer (Figure 3, (c)). As the reaction is highly kinetically controlled, in contrast to the equilibrium nature of metathesis, unsymmetric products are also accessible.^[9] For some industrially relevant polycondensations, like polyamide synthesis, diacid monomers are preferred over the diesters. Long-chain diacids are also accessible from unsaturated fatty acids directly by isomerizing hydroxycarbonylation.^[10]

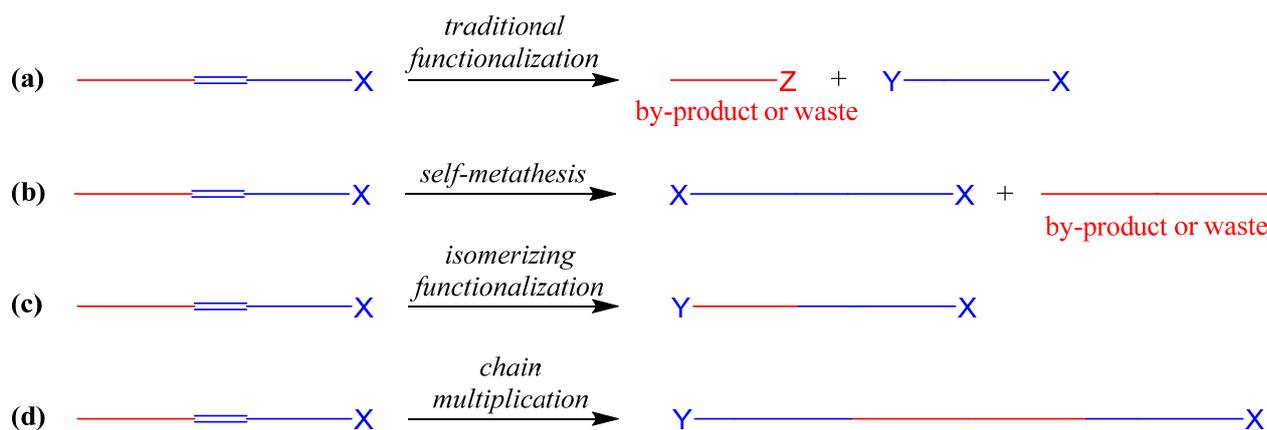


Figure 3. Schematic representation of functionalization of unsaturated fatty acids (left) to α,ω -difunctional molecules. X: carboxylate group of fatty acid substrate, Y and Z: newly generated functional groups (after subsequent double bond hydrogenation for the case of self-metathesis and chain multiplication).

Notably, all the aforementioned methods are compatible with real-life technical grade plant oil feedstocks.^[4,11] Even larger building blocks that exceed the length of a fatty acid chain (Figure 3, (d)) are accessible by ‘chain multiplication’ of common unsaturated fatty acids.^[12] This fully catalytic, iterative scheme is based on a dynamic catalytic isomerizing crystallization in combination with an olefin metathesis step (Figure 4). With erucic acid as a substrate, the ultralong-chain linear C_{48} diacid is generated in high purity and yield. Notably, as these molecules themselves already crystallize like polyethylene, they can be considered as polyethylene telechelics.^[12,13]

The (ultra)long-chain α,ω -dicarboxylates can be reduced to the corresponding diols cleanly, most elegantly by catalytic reduction with dihydrogen.^[8] These diols in turn can be converted to long-chain α,ω -diamines, by catalytic reaction with ammonia,^[14,15] in a purity suited for polycondensation to long-chain polyamides.^[15]

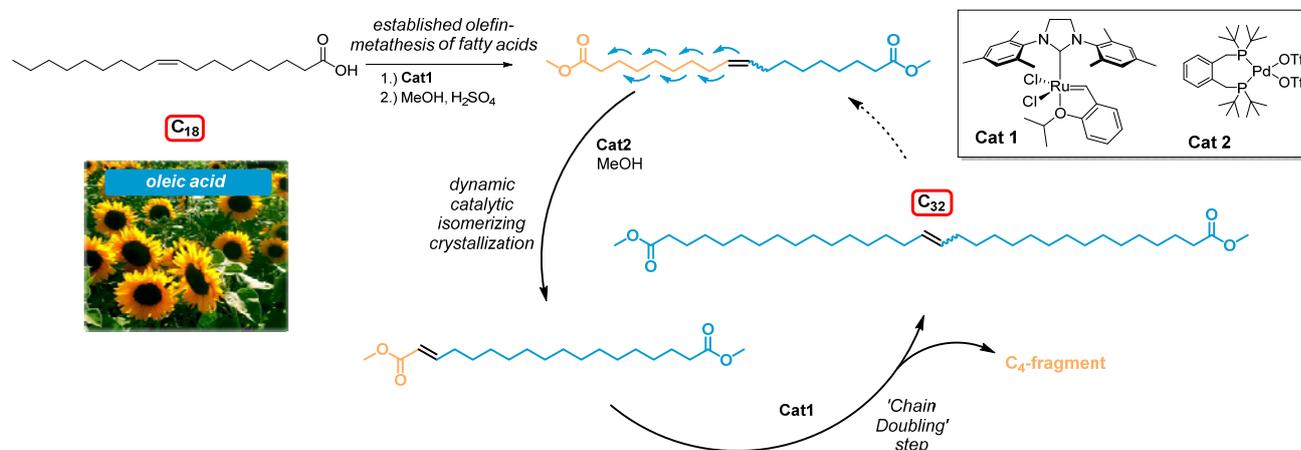


Figure 4. ‘Chain doubling’ approach, illustrated for oleate as a starting material. Adapted from ref. [12].

Considering the plant oil feedstocks used, microalgae oils are of great promise. They do not require arable land, and microalgae can grow rapidly, contain high lipid yields, and do not demand fresh water. While these advantages have long been recognized, to date the efficiency of algae growth and work up represent limitations. As an aside, a future availability of low cost electric energy could be a decisive parameter. Current commercial uses of microalgae lipids comprise the production of high value pharmaceuticals and nutrition supplements. On the other hand, the technical feasibility of fuel production from microalgae has been demonstrated in government-sponsored programmes. This production of fuel usually comprises a defunctionalisation to hydrocarbons, similar to the ones produced from crude oil. A production of higher value chemicals that make use of the unique microalgae fatty acids’ molecular structure appears more sensible.^[16] To this end, the aforementioned catalytic routes to long-chain monomers from seed oils have also been demonstrated and adapted to microalgae oils.^[17,18] This can also provide monomers with chain lengths not accessible from seed oils. The extraction of the desired feedstocks is an ubiquitous bottleneck in the utilization of biomass. An approach to relieve this problem and simplify the overall process scheme is integration of the extraction and catalytic upgrading.^[19] By adopting the conditions

used in both steps, like solvents employed, intermediate work up procedures can be simplified or omitted altogether. Supercritical carbon dioxide is a medium of choice for this concept.^[20]

3 Materials

The establishment of viable routes to (ultra)long-chain monomers enabled studies of corresponding polymers, with characteristic long sequences of methylene groups in their main chains.^[21] The perhaps most prominent example are polyesters, obtained by titanium-alkoxide catalysed polycondensation of long chain linear dicarboxylic acids (or esters) and diols. The high monomer purity, together with a suitable polymerization protocol, enables the attainment of sufficiently high molecular weights of typically M_n 20.000 g mol⁻¹ to > 70.000 g mol⁻¹. Thus, even film extrusion was possible (Figure 5, left image). Injection molded specimens show tensile properties matching those of polyethylenes.^[22] The long-chain aliphatic segments can also serve as hard blocks in thermoplastic elastomers (TPEs), as demonstrated for polyester and polyurethane TPEs.^[23,24] Note that ring opening polymerization of fatty acid-derived macrolactones is an alternative route to long-chain polyesters.^[25] As a chain growth reaction it potentially can yield even higher molecular weights than the aforementioned polycondensations, should this turn out to be required. A drawback is the less straightforward access to the monomers.

The thermal properties and solid state structures of materials are decisive for their applications and processing properties. How are they impacted by the functional groups in the hydrocarbon chains? To this end, model polymers were also prepared by acyclic diene metathesis copolymerization (ADMET). This provides, after hydrogenation, polymers with easily variable and very low densities of functional groups in a polyethylene chain. Wide angle x-ray scattering (WAXS) on these model polymers, and on the aforementioned polymers from polycondensation of long-chain dicarboxylates or diols, show identical patterns and unit cells as observed for HDPE. The functional ester, carbonate and various other groups can be accommodated in the polyethylene crystal lamella.^[26,27,28] Thus, they will be located in the amorphous but also in the crystalline portions. The latter goes along with an energy penalty, which accounts for the lower melting points compared to HDPE (the effect of possible changes in lamella thickness is essentially negligible^[29]). Polyacetals deviate from this picture in that accommodation in the crystals is hindered due to the conformations of acetal groups not being compatible with an all-trans arranged methylene chain.^[28,30]

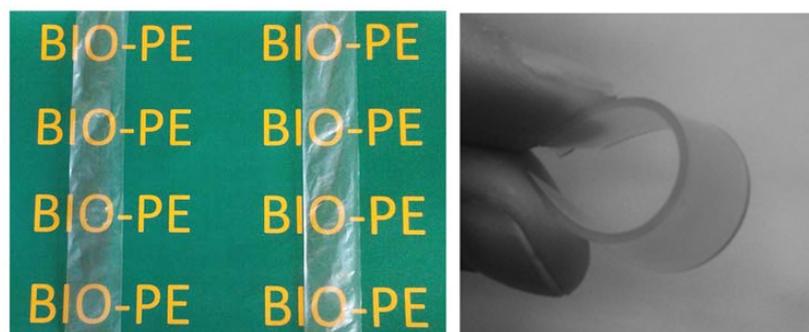


Figure 5. Left image: Melt-extruded films of polyester-19.19 $[\text{OOC}(\text{CH}_2)_{17}\text{COO}(\text{CH}_2)_{19}]_n$ (left) and polyester-23.23 (right). Reprinted from [22]. Published by the Royal Society. Right image: Injection-molded specimen of poly(octatetracontane H-phosphonate). Reprinted with permission from [34]. Copyright 2017 American Chemical Society.

Regarding their potential hydrolytic degradation, these materials are particular in that they contain hydrolysable groups in the main chain – in some cases groups which can be hydrolysed very easily – but at the same time are semicrystalline and largely hydrophobic hydrocarbons. Thus, acetals are usually easily hydrolysed.^[31] The aforementioned long-chain polyacetals $[(\text{CH}_2)_x\text{OCH}_2\text{O}]_n$ ($x = 18, 19, \text{ or } 23$) by contrast appear stable under aqueous conditions, and a notable weight loss in short term experiments of two to four weeks requires forcing acidic or basic conditions. Heise et al. reported that upon exposure to neutral aqueous conditions of polyester-15, no weight loss was observable over a year.^[32] Wurm et al. reported that long-chain poly(orthoesters) (prepared from multistep petrochemical monomers) were not composted, but briefly noted possible evidence for hydrolysis on exposure of polymer powder to air for six months.^[33] Overall, knowledge of the hydrolytic degradation behaviour of these polyethylene-like polymers is patchy. Notably, beyond compostable materials there is a certain lack of standardized protocols for testing degradability of polymer materials. Weight loss in such experiments is a crude measure and requires an advanced degradation. Longer term experiments capturing mechanical properties and surface erosion in the optional presence of microorganisms are necessary. With regard to the question whether the functional groups can be accessed efficiently at all by water to allow for a rapid degradation of such hydrophobic materials, poly(H-phosphonates) are instructive. Pellets of $[(\text{CH}_2)_x\text{OP}(\text{H})=\text{O}]_n$ with ultra-long methylene chains originating from PE-telechelics ($x = 48$) (cf. Figure 5, right image) under aqueous conditions gradually degrade to the monomers over a few days.^[34]

4 Outlook

An important next step is meaningful studies of the degradation of these polyethylene-like materials to assess their persistency behaviour under environmental conditions, including marine environments. Such studies should also include insights on the fate of fragments with sizes in the micron- or nanoscale regime. An understanding of how the accessibility of the hydrolysable in-chain functional groups relates to the morphology of these hydrophobic crystalline materials is required. An exploration and tailoring of the materials properties to non-traditional processing methods and applications is also attractive. Beyond the approach discussed here, advanced polymerization procedures and catalysts can provide alternative approaches to degradable polyolefin materials.

Additional Information

Acknowledgments

I would like to acknowledge my coworkers, not only for their essential role in the results reviewed here but also for the very enjoyable everyday work climate. Past and ongoing funding of this work by the Alexander von Humboldt-Foundation, BASF, the Baden-Württemberg Foundation, the Carl-Zeiss-Foundation and the European Research Council is gratefully acknowledged.

Competing Interests

I have no competing interests.

References

-
- [1] G. Strobl. 2007. The Physics of Polymers. Concepts for Understanding their Behaviour and Structures. 3rd Edn., Springer, Berlin. ([doi](#))
- [2] International Energy Agency. 2017. World Energy Outlook. ([doi](#))
- [3] M. Genas. 1962. Rilsan (Polyamid 11), Synthese und Eigenschaften. *Angew. Chem.* **74**, 535–540. ([doi](#))
- [4] S. Chikkali, S. Mecking. 2012. Refining of Plant Oils to Chemicals by Olefin Metathesis. *Angew. Chem. Int. Ed.* **51**, 5802–5808. ([doi](#))
- [5] V. Goldbach, P. Roesle, S. Mecking. 2015. Catalytic Isomerizing ω -Functionalization of Fatty Acids. *ACS Catal.* **5**, 5951–5972. ([doi](#))
- [6] P. Roesle, L. Caporaso, M. Schnitte, V. Goldbach, L. Cavallo, S. Mecking. 2014. A Comprehensive Mechanistic Picture of the Isomerizing Alkoxyacylation of Plant Oils. *J. Am. Chem. Soc.* **136**, 16871 - 16881. ([doi](#))
- [7] D. Quinzler, S. Mecking. 2010. Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization. *Angew. Chem. Int. Ed.* **49**, 4306–4308. ([doi](#))
- [8] F. Stempfle, D. Quinzler, I. Heckler, S. Mecking. 2011. Long-Chain Linear C₁₉ and C₂₃ Monomers and Polycondensates from Unsaturated Fatty Acid Esters. *Macromolecules* **44**, 4159 - 4166. ([doi](#))
- [9] T. Witt, F. Stempfle, P. Roesle, M. Häußler, S. Mecking. 2015. Unsymmetrical α,ω -Difunctionalized Long-Chain Compounds via Full Molecular Incorporation of Fatty Acids. *ACS Catal.* **5**, 4519 – 4529. ([doi](#))
- [10] V. Goldbach, L. Falivene, L. Caporaso, L. Cavallo, S. Mecking. 2016. Single Step Access to Long-Chain α,ω -Dicarboxylic Acids by Isomerizing Hydroxyacylation of Unsaturated Fatty Acids. *ACS Catal.* **6**, 8229 – 8238. ([doi](#))
- [11] M. R. L. Furst, R. Le Goff, D. Quinzler, S. Mecking, C. H. Botting, D. J. Cole-Hamilton. 2012. Polymer Precursors from Catalytic Reactions of Natural Oils. *Green Chem.* **14**, 472 - 477. ([doi](#))
- [12] T. Witt, M. Häußler, S. Kulpa, S. Mecking. 2017. Chain Multiplication of Fatty Acids to Precise Telechelic Polyethylene. *Angew. Chem. Int. Ed.* **56**, 7589 – 7594. ([doi](#))
- [13] L. Yan, M. Häußler, J. Bauer, S. Mecking, K. Winey. 2019. Monodisperse and Telechelic Polyethylenes Form Extended Chain Crystals with Ionic Layers. *Macromolecules* **52**, 4949 – 4956. ([doi](#))
- [14] G. Walther, J. Deutsch, A. Martin, F. E. Baumann, D. Fridag, A. Köckritz. 2011. α,ω -Functionalized C₁₉ Monomers. *ChemSusChem* **4**, 1052–1054. ([doi](#))
- [15] D. Pinggen, J. B. Schwaderer, J. Walter, J. Wen, G. Murray, D. Vogt, S. Mecking, 2018. Diamines for Polymer Materials via Direct Amination of Lipid- and Lignocellulose-based Alcohols with NH₃. *ChemCatChem* **10**, 3027–3033. ([doi](#))
- [16] S. K. Hess, B. Lepetit, P. G. Kroth, S. Mecking. 2018. Production of Chemicals from Microalgae Lipids – Status and Perspectives. *Eur. J. Lipid Sci. Techn.* **120**, 1700152. ([doi](#))
- [17] P. Roesle, F. Stempfle, S. K. Hess, J. Zimmerer, C. Río Bártulos, B. Lepetit, A. Eckert, P. G. Kroth, S. Mecking. 2014. Synthetic Polyester from Algae Oil. *Angew. Chem. Int. Ed.* **53**, 6800 – 6804. ([doi](#))
- [18] S. K. Hess, N. S. Schunck, V. Goldbach, D. Ewe, P. Kroth, S. Mecking. 2017. Valorization of Unconventional Lipids from Microalgae or Tall oil via a Selective Dual Catalysis One-pot Approach. *J. Am. Chem. Soc.* **139**, 13487–13491. ([doi](#))
- [19] D. Pinggen, N. Klinkenberg, S. Mecking. 2018. Single-Step Catalytic Upgrading of Microalgae-Biomass. *ACS Sustainable Chem. Eng.* **6**, 11219–11221. ([doi](#))
- [20] J. Zimmerer, D. Pinggen, S. K. Hess, T. Köngeter, S. Mecking. 2019. Integrated Extraction and Catalytic Upgrading of Microalgae Lipids in Supercritical Carbon Dioxide. *Green Chem.* **21**, 2428–2435. ([doi](#))
- [21] F. Stempfle, P. Ortmann, S. Mecking. 2016. Long-Chain Aliphatic Polymers to Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates. *Chem. Rev.* **116**, 4597–4641. ([doi](#))
- [22] F. Stempfle, B. S. Ritter, R. Mülhaupt, S. Mecking. 2014. Long-Chain Aliphatic Polyesters from Plant Oils for Injection Molding, Film Extrusion and Electrospinning. *Green Chem.* **16**, 2008–2014. ([doi](#))
- [23] F. Stempfle, B. Schemmer, A.-L. Oechsle, S. Mecking. 2015. Thermoplastic Polyester Elastomers based on Long-Chain Crystallizable Aliphatic Hard Segments. *Polym. Chem.* **6**, 7133–7137. ([doi](#))
- [24] B. Schemmer, C. Kronenbitter, S. Mecking. 2018. Thermoplastic Polyurethane Elastomers with Aliphatic Hard Segments Based on Plant-oil Derived Long-Chain Diisocyanates. *Macromol. Mater. Eng.* **303**, 1700416. ([doi](#))
- [25] D. Myers, T. Witt, A. Cyriac, M. Bown, S. Mecking, C. K. Williams. 2017. Ring Opening Polymerization of Macrolactones: High Conversions and Activities Using an Yttrium Catalyst. *Polym. Chem.* **8**, 5780–5785. ([doi](#))

-
- [26] M. G. Menges, J. Penelle, C. Le Fevere de Ten Hove, A. M. Jonas, K. Schmidt-Rohr. 2007. Characterization of Long-Chain Polyesters: Crystalline and Supramolecular Structure of PE22,4 Elucidated by X-Ray Scattering and Nuclear Magnetic Resonance. *Macromolecules* **40**, 8714–8725. ([doi](#))
- [27] P. Ortmann, S. Mecking. 2013. Long-Spaced Aliphatic Polyesters. *Macromolecules* **46**, 7213–7218. ([doi](#))
- [28] P. Ortmann, I. Heckler, S. Mecking. 2014. Physical Properties and Hydrolytic Degradability of Polyethylene-Like Polyacetals and Polycarbonates. *Green Chem.* **16**, 1816–1827. ([doi](#))
- [29] M. P. F. Pepels, M. R. Hansen, H. Goossens, R. Duchateau. 2013. From Polyethylene to Polyesters: Influence of Ester Groups on the Physical Properties. *Macromolecules* **46**, 7668–7677. ([doi](#))
- [30] X. Zhang, X. Zuo, P. Ortmann, S. Mecking, R. G. Alamo. 2019. Crystallization of Long-Spaced Precision Polyacetals. I: Melting and Recrystallization of Rapidly Formed Crystallites. *Macromolecules* **52**, 4934–4948. ([doi](#))
- [31] B. Laycock, M. Nikolic, J. M. Cowell, E. Gauthier, P. Halley, S. Bottle, G. George. 2017. Lifetime Prediction of Biodegradable Polymers. *Progr. Polym. Sci.* **71**, 144–189. ([doi](#))
- [32] I. van der Meulen, M. de Geus, H. Antheunis, R. Deumens, E. A. J. Joosten, C. E. Koning, A. Heise. 2008. Polymers from Functional Macrolactones as Potential Biomaterials: Enzymatic Ring Opening Polymerization, Biodegradation, and Biocompatibility. *Biomacromolecules* **9**, 3404–3410. ([doi](#))
- [33] T. Haider, O. Shyshov, O. Suraeva, I. Lieberwirth, M. von Delius, F. R. Wurm. 2019. Long-Chain Polyorthoesters as Degradable Polyethylene Mimics. *Macromolecules* **52**, 2411–2420. ([doi](#))
- [34] H. Busch, E. Schiebel, A. Sickinger, S. Mecking. 2017. Ultra-Long-Chain Spaced Crystalline Poly(H-phosphonate)s and Poly(phenylphosphonate)s. *Macromolecules* **50**, 7901–7910. ([doi](#))