Plant oil renewable resources as green alternatives in polymer science

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The utilization of plant oil renewable resources as raw materials for monomers and polymers is discussed and reviewed. In an age of increasing oil prices, global warming and other environmental problems (e.g. waste) the change from fossil feedstock to renewable resources can considerably contribute to a sustainable development in the future. Especially plant derived fats and oils bear a large potential for the substitution of currently used petrochemicals, since monomers, fine chemicals and polymers can be derived from these resources in a straightforward fashion. The synthesis of monomers as well as polymers from plant fats and oils has already found some industrial application and recent developments in this field offer promising new opportunities, as is shown within this contribution. (138 references.)

Introduction

The use of renewable raw materials can significantly contribute to a sustainable development,[1] usually interpreted as "acting responsibly to meet the needs of the present without compromising the ability of future generations to meet their own needs".[2] In ages of depleting fossil oil reserves and an increasing emission of green house gases it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development. In particular, this can perennially provide a raw material basis for daily life products and avoid further contribution to green house effects due to CO_2 emission minimization. Furthermore, the utilization of renewable raw materials, taking advantage of the synthetic potential of nature, can (in some cases) meet other principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products.[1]

Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (mainly cellulose and starch), sugars,

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Michael A. R. Meier was born in Ingolstadt (Germany) in 1975. He graduated in chemistry from the University of Regensburg (Germany) in 2002. His diploma thesis dealt with the fluorosensing of ammonium ions via molecular recognition and was carried out at the University of Regensburg with Prof. O. Wolfbeis. In July 2006 he finished his PhD thesis with Prof. U. S. Schubert at the Eindhoven University of Technology, The Netherlands, in the fields of combinatorial polymer research and supramolecular materials, which was awarded with the Golden Thesis Award 2006 from the Dutch Polymer Institute (DPI). Afterwards he continued to work as DPI project leader in the same fields in Eindhoven. In October 2006 he was appointed principal investigator of the junior research group "Renewable Raw Materials" at the University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven, where his work focuses on the synthesis of novel monomers, polymers as well as fine
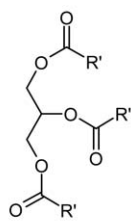
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chemicals utilizing plant oils as renewable raw materials. Besides this appointment he will continue his activities as DPI project leader.

Jürgen O. Metzger, born in 1940, studied chemistry in Tübingen, Erlangen, Berlin, and Hamburg. He gained his doctorate at the University of Hamburg in 1970 on Ziegler–Natta catalysts with H. Sinn and his habilitation at the University of Oldenburg in 1983 on the topic "Thermally initiated intermolecular organic reaction at elevated temperatures and pressures, and reactions under supercritical conditions". In 1991 he was appointed Professor of Organic Chemistry. His work areas include sustainability in chemistry, environmentally benign organic synthesis, renewable raw materials, radical chemistry, and mass spectrometry. He retired in 2006. Since 2006 he has been chairman of abiosus e.V., a non-profit association for the advancement of research on renewable raw materials.

Jürgen O. Metzger

R (x,y) =	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:0
new rapeseed	-	-	0.5	4	1	60	20	9	2
sunflower	-	-	-	6	4	28	61	-	-
palm kernel	5	50	15	7	2	15	1	-	-
linseed	-	-	-	5	4	22	15	52	-
soy	-	-	-	10	5	21	53	8	0.5

Fig. 1 Left: Chemical structure of triglycerides. Right: Typical compositions of industrially important plant oils in % (R (x:y) = composition of the fatty acids; x = chain length in carbon atoms; y = number of double bonds). (Important notes: numbers do not add to 100%; R ≠ R').

wood, and others. Products obtained from these renewables are as diverse as pharmaceuticals, coatings, packaging materials or fine chemicals, to only name a few. Moreover, recent discussions focus on the gasification of biomass (e.g. wood, wood wastes, corn stover, switch grass, agricultural waste, straw or others) with temperature, pressure and oxygen to obtain syngas[3] (mainly consisting of CO and H_2) and subsequent Fischer–Tropsch synthesis to obtain higher hydrocarbons. Alternatively, the obtained syngas can be converted to methanol and the thus obtained alcohol could contribute to the "methanol economy" as discussed by Nobel laureate George A. Olah and co-authors.[4] In both approaches biomass can be used as fuel but can also serve as renewable feedstock for the chemical industry.

Today plant oils are the most important renewable raw material for the chemical industry (e.g., in Germany 30% of the 2.7 million tons of renewable raw materials in 2005 were plant oils; in total approximately 10% of all resources were renewable) and are heavily used as raw materials for surfactants, cosmetic products, and lubricants.[5] In addition, plant oils have been used for decades in paint formulations, as flooring materials and for coating and resin applications. The probably best known application example is Linoleum, which was already industrially produced in 1864 and developed by F. Walton in London, UK.[6,7] Its main component is linseed oil and it provides a durable and environmentally friendly alternative to, e.g., PVC floorings.

Plant oils are triglycerides (tri-esters of glycerol with long-chain fatty acids, see Fig. 1) with varying composition of fatty acids depending on the plant, the crop, the season, and the growing conditions.[8] The word 'oil' hereby refers to triglycerides that are liquid at room temperature. The most important parameters affecting the physical and chemical properties of such oils are the stereochemistry of the double bonds of the fatty acid chains, their degree of unsaturation as well as the length of the carbon chain of the fatty acids. The degree of unsaturation, which can be expressed by the iodine value (amount of iodine in g that can react with double bonds present in 100 g of sample under specified conditions) can be used as a simple parameter to divide oils into three classes: drying (iodine value >170; e.g. linseed oil), semi-drying (100< iodine value <170; e.g. sunflower or soy oils) and non-drying (iodine value <100; e.g. palm kernel oil) oils.[7] In terms of fatty acid composition, linseed oil, for instance, mainly consists of linolenic (all-cis-9,12,15-octadecatrienoic acid) and linoleic acid (all-cis-9,12-octadecadienoic acid), whereas in castor oil, the most abundant fatty acid is ricinoleic acid ((9Z,12R)-12-hydroxy-9-octadecenoic acid), providing additional natural chemical functionality for modifications, cross-linking or polymerization. Fig. 1 summarizes the chemical composition of some industrially important plant oils. From Fig. 1, it can for instance be seen that new rapeseed oil is rich in oleic acid (R = 18:1), whereas palm kernel oil is rich in lauric acid (R = 12:0).

For a more complete overview and for reasons of easier reading and understanding, Fig. 2 displays an overview of interesting fatty acids for chemical modification and the synthesis of fine chemicals, monomers and polymers. Approximately 80% of the global oil and fat production is vegetable oil, whereas 20% is of animal origin (share decreasing).[9] About 25% is soybean, followed by palm oil, rapeseed, and sunflower oil. Coconut and palm kernel oil (laurics) contain a high percentage of saturated C12 and C14

Ulrich S. Schubert

Ulrich S. Schubert was born in Tübingen in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth (both Germany) and the Virginia Commonwealth University, Richmond (USA). His PhD work was performed under the supervision of Professor Eisenbach (Bayreuth, Germany) and Professor Newkome (Florida, USA). After a postdoctoral training with Professor Lehn at the Université Strasbourg (France) he moved to the Technische Universität München (Germany) to obtain his habilitation in 1999 (with Professor Nuyken). From 1999 to spring 2000 he held a temporary position as a professor at the Center for NanoScience at the Universität München (Germany). From June 2000 to March 2007 he was Full-Professor at the Eindhoven University of Technology (Chair for Macromolecular Chemistry and Nanoscience). Since April 2007 has been Full-Professor at the Friedrich-Schiller-University Jena (Chair of Organic and Macromolecular Chemistry) and Part-time Professor in Eindhoven. His awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Makromolekulare Chemie), the Heisenberg-Stipendium of the DFG and the Dozenten-Stipendium of the Fonds der Chemischen Industrie.
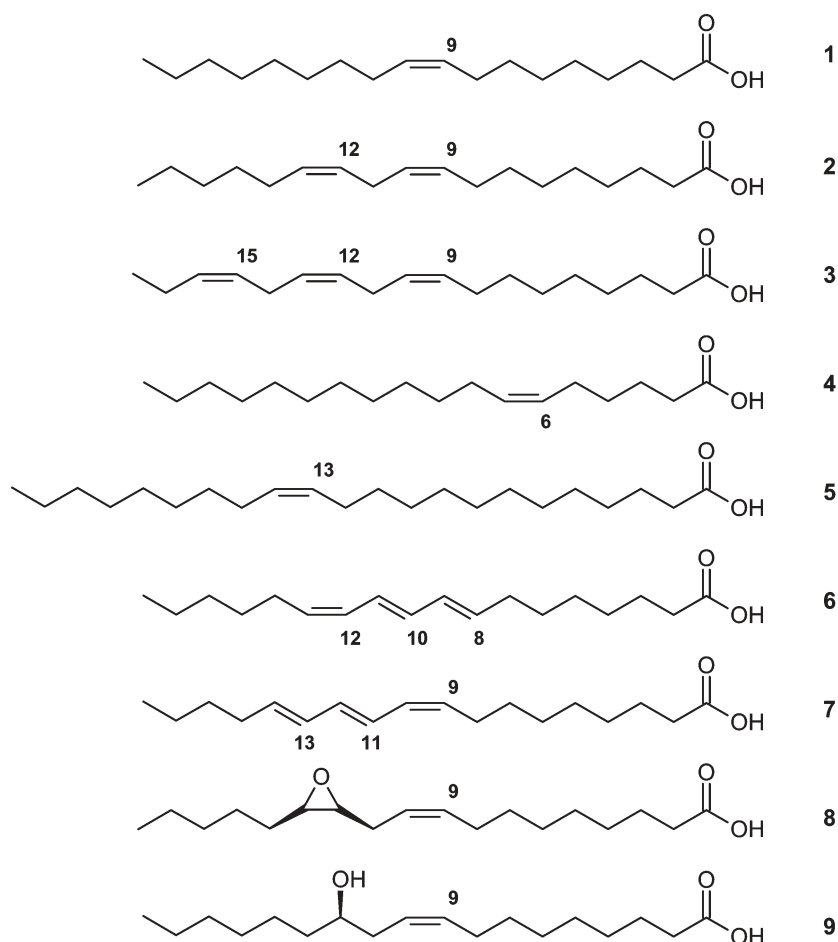
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Fig. 2 Fatty acids as starting materials for the synthesis of novel fatty compounds: (**1**) oleic acid, (**2**) linoleic acid, (**3**) linolenic acid, (**4**) petroselinic acid, (**5**) erucic acid, (**6**) calendic acid, (**7**) α-eleostearic acid, (**8**) vernolic acid, (**9**) ricinoleic acid.[9]

fatty acids (compare Fig. 1) and are most important for the production of surfactants. These commodity oils make highly pure fatty acids available that may be used for chemical conversions and for the synthesis of chemically pure compounds such as oleic acid (**1**) from "new sunflower," linoleic acid (**2**) from soybean, linolenic acid (**3**) from linseed, erucic acid (**5**) from rapeseed, and ricinoleic acid (**9**) from castor oil (see Fig. 2).[9]

Recently, the application of triglycerides in polymer science was reviewed with a focal point on cross-linked systems for coating and resin applications with the conclusion that triglycerides are expected to play a key role during the 21st century to synthesize polymers from renewable sources.[10] In addition to these cross-linked systems, linear, processable polymers can also be obtained from plant oils. Within this contribution, we want to provide an overview of the field by highlighting and discussing the current state-of-the-art as well as selected perspectives of the utilization of plant oil renewable resources in polymer science. We will thereby only consider triglycerides and their derivatives and will not discuss other chemicals that can be derived from plants, such as limonene, even if these chemicals have also been shown to have an application potential in polymer science. As one prominent example in this area of research, the work of Coates *et al.* can

be pointed out, since they were able to copolymerize CO_2 with limonene oxide (which is derived from limonene, the major component of oils from citrus fruit peels; *e.g.* 95% of the oil from orange peels) with the help of a zinc catalyst to obtain poly(limonene carbonate), that showed many of the characteristics of poly(styrene).[11] We cover both cross-linked and linear systems that are derived from triglyceride oils, including monomer as well as polymer synthesis procedures in order to provide a complete picture and also to allow an easy entry into the topic. A substantial part of this review will then address living and controlled polymerizations, such as anionic polymerization or controlled radical polymerization techniques, since in our opinion these procedures offer the most challenges as well as opportunities in the future. Finally, we will finish our discussions by briefly pointing out the uses of glycerol, a by-product of fatty acid methyl ester production (biodiesel), and by evaluating the sustainability and environmental impact of the discussed approaches.

Cross-linked systems

Direct cross-linking

Drying oils (see introduction for a definition) are characterized by their ability to form resins due to autoxidation, peroxide

formation and subsequent radical polymerization and are therefore applied as binders and film formers in paint and coating formulations. In recent years, this process was studied in detail by Fourier transform infrared spectroscopy (FT-IR) and other spectroscopic techniques[12–15] and new tests to investigate liquid oxy-polymerizations of oils were developed.[16] In particular, it could be shown that cobalt driers accelerate the drying procedure but do not change the polymerization mechanism.[12] This accelerated drying with primary cobalt driers can, however, lead to the formation of a solid surface layer in thick films, while the oil is still viscous under this film. Therefore, a poor through-dry can be one of the major drawbacks of drier use.[12] Moreover, the curing behaviors of linseed and poppyseed oils at 60 °C have been studied by FT–IR as well as Fourier-transform Raman spectroscopy resulting in the identification of additional reaction intermediates and a better understanding of the overall (rather complicated) mechanism.[13] These studies revealed and confirmed that, after the well understood initial reaction step of an abstraction of a bisallylic hydrogen atom and trapping of the radical by oxygen followed by hydrogen abstraction leads to the formation of hydroperoxides,[17] the curing proceeds by isomerization of the double bonds, C–C-bond scission giving alcohol, aldehyde, saturated and unsaturated ketone as well as carboxylic acid, perester and γ-lactone functionalities.[13,17] Subsequently, the curing continues as evidenced by a rapid decrease in the double bond concentration as well as epoxide formation. Recombination reactions between the formed radicals (*e.g.* alkyl, alkoxyl, and peroxyl radicals) are responsible for the cross-linking and the accompanying increase in viscosity and molecular weight. A simplified scheme of the overall cross-linking reaction of drying oils is provided in Fig. 3. These reactions are the explanation why unmodified oils and fats with a high iodine value are valuable materials in painting formulations or resin applications.

Additionally, it was reported that oils with high iodine value can be polymerized directly *via* cationic polymerization, initiated for example by boron trifluoride diethyl etherate.[18,19]

In this respect, the cationic copolymerization of regular soybean oil, low-saturation soybean oil (LoSatSoy), or conjugated LoSatSoy oil with styrene and divinylbenzene provided polymers ranging from soft rubbers to hard, tough, or brittle plastics.[18,19] Moreover, cationic polymerization in scCO$_2$ was performed to obtain polymers with molecular weights ranging from 1 to 23 kDa and application possibilities as lubricants or hydraulic fluids.[20]

Resins from plant oil derivatives

In addition to the direct polymerization of plant oils several methods for the (co)-polymerization of triglycerides and fatty acid derivatives have been developed. Some of the more prominent examples include polyester alkyd resins (see below), polyurethanes, polyamides, epoxy resins, and vinyl copolymers as recently discussed in the literature.[10] The following discussions do not aim to review all literature on these topics, but address briefly some basics and recent developments of the mentioned polymer systems to provide an overview and offer an easy level entry with interesting details, where appropriate, for the reader.

Alkyd resins

Alkyd resins, a class of polyester coatings derived from the reaction of a polyol, a polyvalent acid or acid anhydride, and fatty acid derivatives, are probably one of the oldest applications of plant oil renewable resources in polymer science. The first polyester resin, the condensation product of glycerol with tartrate, was already synthesized in 1847 by Berzelius, whereas Kienle, using syllables from the reactants alcohol and acid, introduced the word *alkyd*.[21] Moreover, he made an alkyd of ethylene glycol, phthalic anhydride and drying oils to obtain linear polymers that could undergo autoxidation polymerization (see above) to obtain air drying products.[21] Today, alkyd resins are typically manufactured from acid anhydrides such as phthalic anhydride or maleic anhydride and polyols such as glycerol or pentaerythritol and are modified with unsaturated fatty acids to give them air
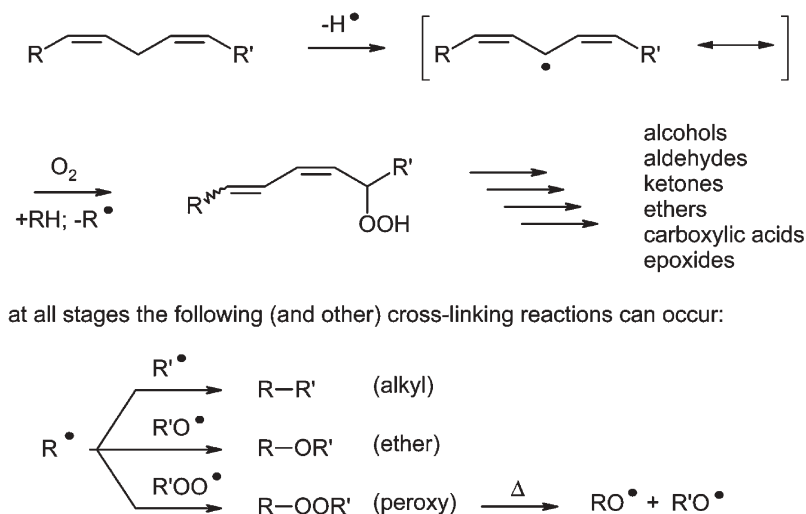

Fig. 3 First reaction steps of the autoxidation of drying oils and the subsequent cross-linking of the material.
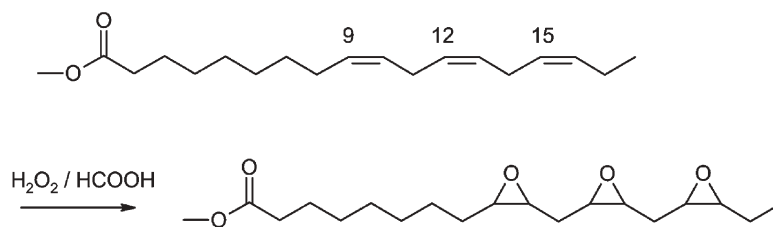
Fig. 4 Epoxidation of methyl linolenate by the performic acid process.

drying properties. This review will not address these materials in further detail, but refers the reader to a recent review article focusing on alkyd resins from renewable raw materials.[22]

Epoxy resins

Probably the most frequently studied polymerization involving plant oils and their derivatives in recent years has been the epoxy resin formation with epoxidized plant oils and fatty acids. The epoxidation of unsaturated fatty acids or triglycerides can be achieved in a straightforward fashion by reaction with, *e.g.*, molecular oxygen, hydrogen peroxide as well as by chemo-enzymatic reactions.[23] Fig. 4 displays the so called *in situ* performic acid process, which is the most widely applied process in industry, for methyl linolenate as an example.[75]

Recently, the epoxidation of soybean oil and the extent of side reactions were studied in the presence of an ion exchange resin as the catalyst and revealed that the reactions were first-order with respect to the double bond concentration and that side reactions did not occur on a large scale.[24] Moreover, a model that predicts the epoxidation kinetics of oils based on their fatty acid composition was derived that closely matched experimental results.[25] Interestingly, it was for instance observed that the rate constants of epoxidation for fatty acid methyl esters increased as the level of unsaturation increased.[25] This process can also be applied to native oils yielding important raw materials for epoxy resins as well as for polyols. These polyols are important raw materials for polyesters as well as polyurethanes. It should be noted here that epoxides can also be polymerized in a living fashion by anionic polymerization allowing the precise adjustment of polymer molecular weights, end-groups as well as polydispersity indices. However, there are no literature examples describing this method applied to fatty acid derivatives resulting in the desired defined polymers. More recently, the catalytic epoxidation of methyl linoleate applying different transition metal complexes as catalysts was studied revealing complete epoxidation using aqueous H_2O_2 (30%) within 4 hours for methyltrioxorhenium (4 mol%) and pyridine.[26] Longer reaction times (6 h) were needed with only 1 mol% catalyst loading. The same catalyst could be successfully applied for the direct epoxidation of soybean oil in a biphasic system showing complete double bond conversion within 2 hours.[27] Moreover, enzymes are presently heavily studied for the epoxidation of plant oils and derivatives, whereby the reaction proceeds *via* the enzymatic *in situ* formation of peracids required for the chemical epoxidation of the double bonds[28–32] and has the general advantage of suppressing undesired ring opening reactions of the obtained epoxides.[23]

The resulting epoxidized plant oil and fatty acid derivatives are valuable materials in polymer science with application possibilities as rubbers, resins or coatings.[33–44] As an example, epoxidized oils with high linolenic acid contents (linseed, Canadian linseed, and the oil of *Lallemantia iberica*) as environmentally friendly cross-linkers for powder coatings were studied revealing a higher degree of yellowing and little influence on the T_g of the powder when compared to the conventionally applied triglycidyl isocyanurate cross-linker.[44] Furthermore, the researches suggested that oil crops with even higher iodine values might lead to a significant increase in T_g of the powders. Cádiz *et al.* could show that monomers derived from 10-undecenoic acid are valuable materials for epoxy resins.[39,45] First, new epoxidized monomers were prepared (compare Fig. 5),[39,45,46] which were subsequently cross-linked with 4,4′–diaminodiphenylmethane (DDM) and *bis*(*m*-aminophenyl)methylphosphine oxide (BAMPO).

Thermosetting materials with moderate T_g values and good thermal stabilities were obtained from these monomers with DDM and BAMPO as hardeners. The presence of phosphorus increased the limiting oxygen indices (LOI: minimum oxygen concentration of an O_2/N_2 mixture required to sustain combustion), demonstrating the efficiency of DOPO-III to act as a reactive flame retardant. Moreover, epoxidized castor oil[36,40,41] (ECO), epoxidized soybean oil[37,41] (ESO) as well as other epoxidized plant oils[38] are currently evaluated for their potential use in epoxy resin applications. The systems developed by Park and Lee *et al.* use thermally latent catalysts (*e.g.* *N*-benzylpyrazinium hexafluoroantimonate or *N*-benzylquinoxalinium hexafluoroantimonate) to initiate the polymerization.[36,40,41] They discovered that different catalysts had an influence on the cross-linking density, which affected the T_g, coefficient of thermal expansion as well as the mechanical properties of the obtained resins.[36] A comparison of ECO and ESO polymerized with these catalysts revealed that ECO provides a higher T_g value and a lower coefficient of thermal expansion, which was attributed to a higher number of intermolecular interactions, such as hydrogen bonding, in the ECO system.[41] Moreover, ESO cured with cyclic acid anhydrides in the presence of tertiary amines also revealed thermoset properties.[37] Interestingly, it was observed that the higher degrees of epoxidation led to higher T_g as well as hardness of the resins. Therefore, it should be possible to obtain epoxy resins with improved properties from oils with even higher iodine values and it would be interesting to study linolenic acid triglyceride as a model material in this respect. Another method to improve the mechanical and other properties of epoxy resins (and other polymers) is the blending
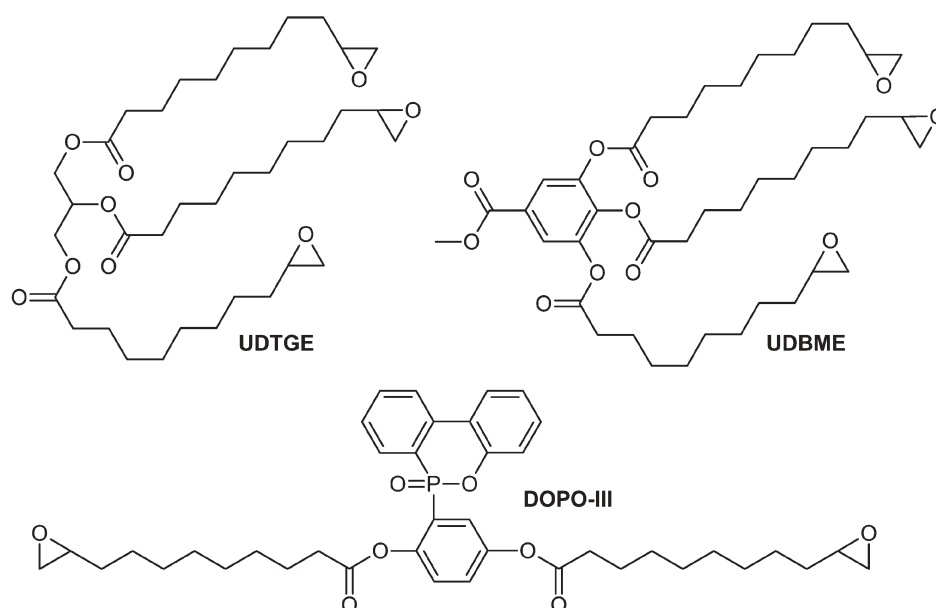
Fig. 5 Structures of epoxidized monomers used for resins.[39,45,46]

with inorganics in order to obtain composite materials. In this respect, epoxidized linseed oil was copolymerized with 3-glycidylpropylheptaisobutyl-T$_8$-polyhedral oligomeric silsesquioxanes (G-POSS) in order to obtain bionanocomposites from renewable resources.[47] Due to the reinforcement with the inorganic POSS derivatives enhanced T_g values and storage moduli of the networks in the glassy state and rubber plateau were observed compared to POSS-free polymers. Moreover, plant oil–clay hybrid materials have been developed by an acid-catalysed curing of epoxidized plant oils (mainly ESO) in the presence of organophilic clay to obtain composites with intercalated and randomly distributed silicate layers within the polymer matrix.[48] Reinforced and still flexible nanocomposites were thus obtained.

Polyurethane resins

Plant oils and their derivatives are also commonly converted into polyols and copolymerized with isocyanates, such as toluenediisocyanate (TDI), methylene-4,4′-diphenyldiisocyanate (MDI) or others, to obtain polyurethanes. In particular, interpenetrating polymer networks from polyurethanes obtained from castor oil and styrenic and/or meth(acrylic) polymers have gained much attention over the last decades due to their interesting properties, as summarized in the literature.[10] Recently, a variety of epoxidized plant oils (canola, midoleic sunflower, soybean, linseed, sunflower and corn) were used to prepare polyols (see Fig. 6).[49]

These polyols were polymerized with MDI revealing that canola, corn, soybean, and sunflower based polyols gave
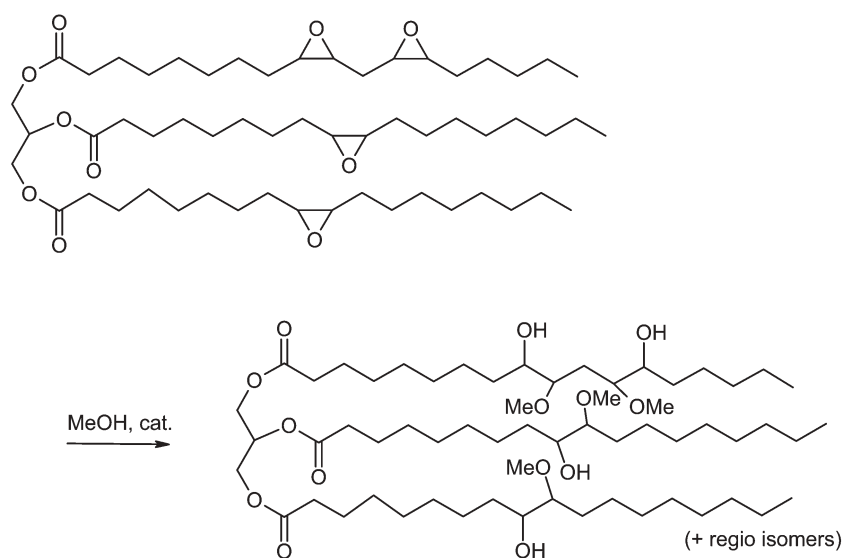

Fig. 6 Polyols prepared for polyurethane synthesis.[49]

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Table 1 Summarized data of polyurethanes (PU) obtained from plant oil derived polyols revealing structure–property relationships[49]

Oil	Iodine value [mg I_2 per 100 g]	OH# of polyol [mg KOH per g]	PU T_g by DCS [°C]	PU tensile strength [MPa]
Canola	114.1	173.6	32	22.9
Midoleic Sunflower	107.6	163.5	24	14.8
Soybean	126.6	179.3	31	20.2
Linseed	182	247.8	77	56.3
Sunflower	133.3	177.8	32	21.7
Corn	125.2	179.0	30	17.7

polyurethane resins of similar cross-linking density (and thus similar T_g) values as well as mechanical properties despite the somewhat different distributions of fatty acids. Higher cross-linking densities and higher mechanical properties were obtained from linseed oil derived polyols, whereas midoleic oil gave softer polyurethanes characterized by lower T_g and lower level of strength but higher elongation at break. Structure–property relationships could be established and the observed properties of the polyurethanes could be correlated to the different hydroxyl values of the used polyols (resulting in different cross-linking densities of the polyurethane networks) and were less dependent on the position of functional groups in the fatty acids of the polyols.[49] Table 1 illustrates these effects and provides more detailed information for the interested reader. Along these lines, Europe's largest flexible foam manufacturer, Recticel, has launched a line of foams that contain Cargill's soybean-oil-based polyols rather than traditional polyols, which are made by reacting propylene oxide with an alcohol. Cargill estimates that replacing 1 million lb of traditional polyols with its soybean-oil-based polyols will save 2,200 barrels of crude oil.[50]

Furthermore, epoxy soy polyols were prepared by a one-step synthesis using a formic acid/H_2O_2 system resulting in polyols
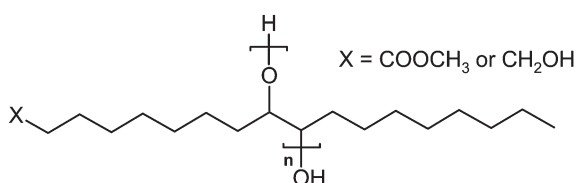
Fig. 7 Polyols prepared by ring opening polymerization of epoxidized methyl oleate and subsequent partial reduction of the esters.[52]
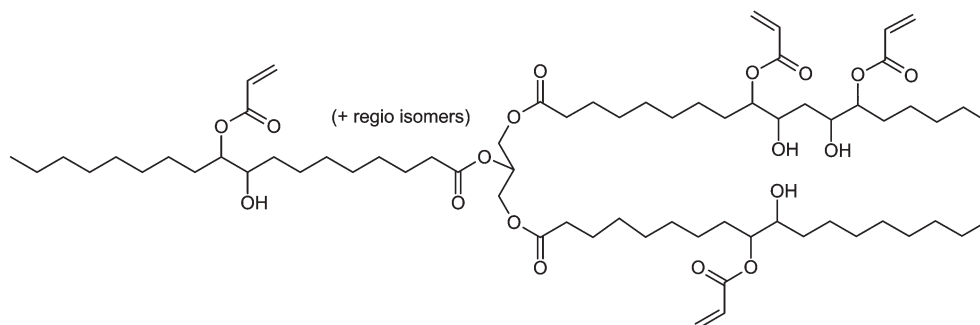
with one OH and one formate group per double bond, and still containing residual epoxy groups.[51] These polyols were reacted with different isocyanates (TDI, MDI as well as HDI: 1,6-hexamethylene diisocyanate) revealing the expected correlation between T_g, cross-linking and OH functionality of the polyols (see above), degrees of swelling in toluene from 1.95 to 3.62 as well as storage moduli in a range from 0.5 to 4 MPa.[51] An interesting approach to obtain novel polyols from plant oil renewable materials was recently described by Lligadas et al. who combined acid-catalysed ring-opening polymerization of epoxidized methyl oleate with a subsequent partial reduction of ester groups to yield oligomeric polyether polyols (Fig. 7).[52] Polymerization of these polyols with MDI yielded materials with varying behavior from hard rubbers to rigid plastics. Moreover, these polyols were used as co-monomers with silicon containing fatty acid derived polyols in the synthesis of silicon containing polyurethanes biobased materials that might be very interesting for applications that require fire resistance.[53]

In a different approach towards polyurethanes fatty acid derivatives were carbonated in supercritical carbon dioxide.[54,55] The resulting cyclic carbonates can be converted to polyurethanes with primary amines avoiding the use of isocyanates (usually phosgene is used for isocyanate synthesis). Recently, such an approach was applied to carbonated soybean oil that was reacted with ethylene diamine, hexamethylenediamine and tris(2-aminoethyl)amine to obtain polyurethane networks with T_g values of approximately 34 °C, 18 °C and 43 °C, respectively.[56]

Other resins (acrylates, acrylamides, maleates, cinamates)

Additionally, acrylated epoxidized soybean oil (AESO, compare Fig. 8) as well as maleinized soy oil monoglyceride and maleinized hydroxylated oil were used to prepare composite materials with glass fibres as well as natural flax and hemp fibres.[57] The obtained materials combined the low cost of natural fibres with the high performance of synthetic glass fibres. Their properties were between those displayed by the all-glass and all-natural composites.

Similar strategies have been applied for the synthesis and (co)-polymerization of monomethyl maleate esters of epoxidized soybean oil (MESO)[58] as well as cinnamate esters of epoxidized soybean oil (ESOCA).[59] Moreover, soybean oil triglycerides were directly reacted with maleic anhydride in an ene reaction to introduce more than two maleate residues per

Fig. 8 Acrylated epoxidized soybean oil monomers used for the preparation of fibre reinforced hybrid materials.[57]

triglycerides.[60] The thus maleinized soybean oil (SOMA) was then polymerized with diols to obtain soft, flexible solids or viscous oily polymers. Moreover, the Ritter reaction with acrylonitrile was applied to plant oil triglycerides in order to obtain acrylamide functional triglycerides.[61] A radical initiated copolymerization of the thus obtained acrylamide derivatives of soybean and sunflower oil with styrene produced semirigid polymers with T_g values of 40 °C and 30 °C, respectively. An additional method to obtain polymerizable plant oil is the bromoacrylation of its double bonds in the presence of acrylic acid and *N*-bromosuccinimide[62] resulting in rigid thermoset polymers from the radical copolymerization of bromoacrylated soybean oil with styrene.[62]

Linear systems

Uncontrolled synthesis

Within this contribution we use the term "uncontrolled" for polymer synthetic methods that do not apply controlled/living polymerization techniques, and thus lead to polymers with broad molecular weight distributions and/or undefined polymer end-groups. Typical examples are step-growth polymerizations or free radical polymerizations, as will be discussed in the following sections.

Polycondensation and polyaddition polymerizations are stepwise reactions of multifunctional monomers with two different reactive groups. The most prominent examples of these polymerizations are the reaction of diacid derivatives (*e.g.* diesters or diacid chlorides) with diols or diamines to yield linear polyesters or polyamides, respectively. Another prominent example is the reaction of diisocyanates with diols to yield linear polyurethanes. If the functionality of one of the monomers is >2 (*e.g.* triols, tetraols) the resulting polymers will possess a branched and ultimately cross-linked architecture, depending on the stoichiometry of the monomers (see previous sections for a discussion of these materials).

Diacid synthesis from plant oil raw materials

Several methods for the synthesis of diacids from fatty acid derivatives are described in the literature.[23,63] In oleochemistry, the industrially most important application of ozonolysis is the oxidation of the double bond of oleic acid to yield azelaic and pelargonic acid (see Fig. 9). Currently, Cognis Oleochemicals is taking advantage of this process on an industrial scale (production approximately 30,000 tonnes per annum) and markets the described bio-based products under the name Ozone acids.[64]

Similarly, the oxidative cleavage can be achieved using tungsten, tantalum, molybdenum, zirconium, and niobium-based catalysts with H_2O_2 in high yields.[65,66] Moreover, the reaction can be performed in a two-step fashion by first *bis*-hydroxylating the double bond with a tungsten catalyst and the subsequent cleavage of the obtained diol with molecular oxygen in the presence of both tungsten and cobalt catalysts[67] or catalytic amounts of *N*-hydroxyphthalimide and Co(acac)$_3$.[68] Generally, due to their long alkyl chains these monomers impart certain properties to the resulting polymers, such as elasticity, flexibility, high impact strength, hydrolytic
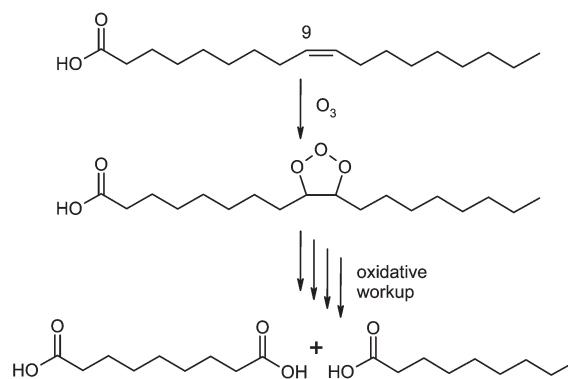
Fig. 9 Ozonolysis of oleic acid to yield azelaic and pelargonic acids.

stability, hydrophobicity, or lower glass transition temperatures.[63] In order to obtain other dimer fatty acids, ricinoleic acid was transformed into a diacid monomer by esterification with maleic or succinic anhydride to yield a nonlinear fatty acid derivative with two or one double bonds, ricinoleic acid maleate (RAM), and ricinoleic acid succinate (RAS), respectively.[69]

Subsequently, hydrogenation of RAS yielded 12-hydroxystearic acid succinate (HSAS, see Fig. 10). Melt condensation polymerization of these monomers yielded polymers with number averaged molecular weights exceeding 40 kDa. These polymers were shown to be biologically inert as well as biodegradable due to rapid hydrolytic degradation and were shown to be applicable for *in vitro* drug release applications.[69]

The resulting polymers should show optical activity due to the natural 12*R* configuration of the used 12-hydroxystearic acid. However, this interesting feature has not yet been studied.

Polyesters

Unsaturated polyesters were, for instance, obtained by a lipase-catalysed synthesis approach.[70] Therefore, divinyl sebacate and glycerol were polymerized regioselectively in a 1,3-addition reaction in the presence of unsaturated fatty acids (*e.g.* linoleic acid) to obtain polyester materials (compare Fig. 11; R′ = fatty acid side chain) that could be cured using a cobalt naphthenate catalyst or by thermal treatment to yield a cross-linked, transparent, polymeric film with a high-gloss surface.[70]

Other polyesters based on fatty acids are so-called estolides.[71–74] Estolides result from ester bond formation between a hydroxyl or olefinic group of one fatty acid and the terminal carboxyl group of a second fatty acid and these products are
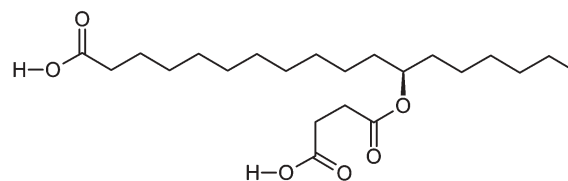
Fig. 10 12-Hydroxystearic acid succinate (HSAS) fatty acid derivative utilized to obtain biodegradable polymers with drug delivery application possibilities.[69]
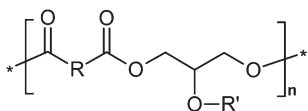
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Fig. 11 Copolyesters obtained by enzymatic copolymerization of divinyl sebacate and glycerol in the presence of unsaturated fatty acids.[70]

Fig. 13 Acrylated epoxidized methyl oleate (AMO) used in emulsion polymerizations.[80]

commonly found in trace amounts in several oil seed plants, but can also be synthesized.[71,72] As an example, estolides prepared from oleic acid are shown in Fig. 12.

These and other estolides are biodegradable and frequently discussed to be applicable as lubricants or in cosmetic products.

Polyamides

Polyamide synthesis from plant oils already found industrial application in the preparation of Nylon-11, since the necessary monomer, 11-amino-undecanioc acid, can be obtained from castor oil (note: 10-undecenoic acid and heptaldehyde can by obtained by pyrolysis of castor oil)[75,76] by further chemical modification of 10-undecenoic acid. Moreover, soy oil based dimer-acids were used as co-monomers in the preparation of co-polyamides with different α-amino acids.[77] It should be noted here that a minor extent of cross-linking was expected from these systems in the case of trifunctional amino acids and due to the presence of small amounts (∼1%) of trimer acids in the soy oil derived dimer acids. However, as argued by the authors, the most likely architecture of their polymers was linear.[77] The introduction of the amino acids into the polymers did not enhance the biodegradation ability but did improve the swelling properties of the co-polyamides in water at a relative high pH and temperature. Moreover, the co-polyamide with L-tyrosine as co-monomer was discussed as easily de-inkeable copy toner revealing that images of these soy-based toners were similar to those of commercially available toners.[78]

Acrylate and methacrylate derivatives

Other monomers based on fatty alcohol acrylates or methacrylates are well known in industry and are applied as low T_g monomers in copolymers of various kinds. However, even though these monomers are well known they have been little studied. A Scifinder™ search performed by registry number for these monomers in January 2007 revealed that surprisingly little scientific literature is available for all alcohol acrylates or methacrylates. Therefore, a detailed study of the polymerization kinetics and (co)-polymerization behavior of these monomers as well as the properties of the resulting polymers
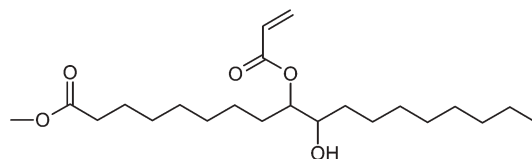
is a prerequisite to close this knowledge gap and to open new avenues for materials with potential applications.

Moreover, several new monomers from plant oils were prepared and polymerized recently. Homo- and co-polymers of bromoacrylated methyl oleate (BAMO) polymers were prepared by thermal as well as photoinitiated free radical polymerization to obtain polymers with number averaged molecular weights (M_n) from 20 to 35 kDa.[79] The determination of the reactivity ratios of BAMO with styrene by the Fineman–Ross as well as Kelen–Tudos methods using ^{1}H-NMR spectroscopic data (r_{sty} = 0.891 (Fineman–Ross), 0.859 (Kelen–Tudos method) and r_{BAMO} = 0.671 (Fineman–Ross method), 0.524 (Kelen–Tudos) indicated, for instance, that styrene polymerized approximately twice as fast as BAMO.[79] Similar monomers, such as acrylated methyl oleate (AMO) as well as methyl oleate acrylamide (MOA), were obtained by acrylation of epoxidized methyl oleate (compare Fig. 13)[80] or the Ritter reaction of methyl oleate and acrylonitrile in the presence of SnCl$_4$,[61,81] respectively.

The sodium salt of MOA, sodium acrylamidostearate (NaAAS), was used as co-monomer resulting in polymeric surfactants with polyelectrolyte behavior which were more surface active than the precursor (NaAAS).[82] AMO, on the other hand, was polymerized by free radical polymerization in emulsion and polymers with high molecular weights (up to 10^6 g mol^{-1}) and high latex solids content were obtained. It was also observed, that high conversion of the AMO led to branched macromolecules due to chain transfer to polymer side-reactions.[80] Similarly, long chain fatty acids have been modified with glycidyl methacrylate and the resulting monomers (see Fig. 14) were discussed as replacements for styrene in vinyl ester resins.[83]

Unfortunately, no data was provided on the polymerization behavior of these monomers applying conventional free radical polymerization to yield linear polymers. Lauryl methacrylate
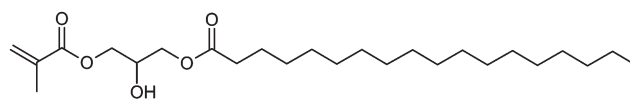

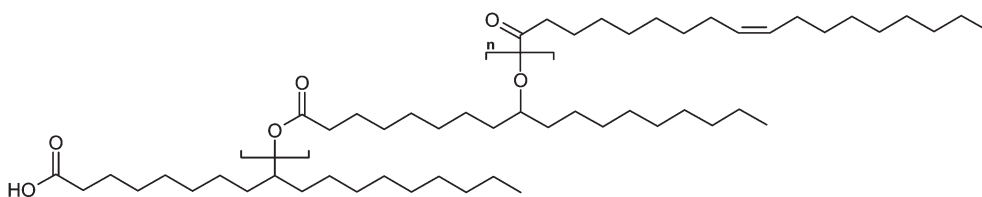**Fig. 14** Methacrylated stearic acid monoglyceride monomer.[83]

Fig. 12 Estolides obtained from oleic acid under acidic conditions.[71]
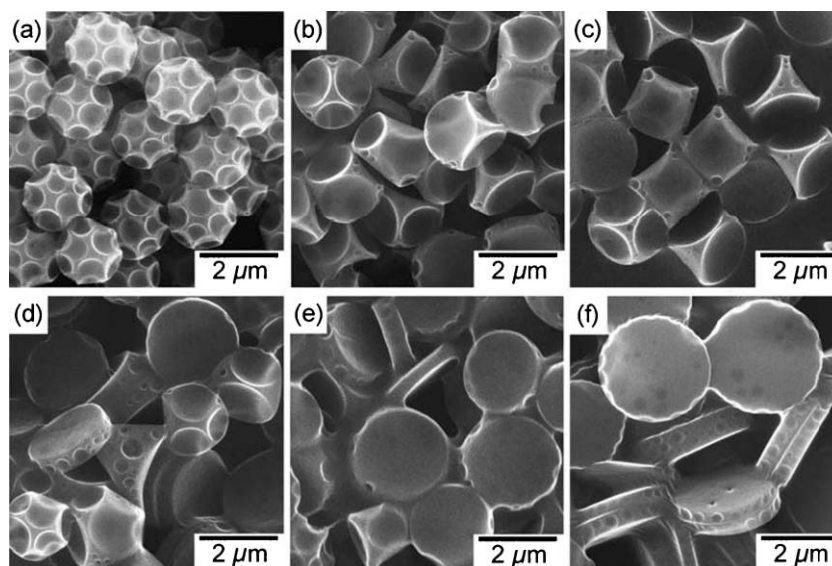
Fig. 15 Scanning electron microscope photographs of PS/poly(lauryl methacrylate) (PLMA) composite particles produced by seeded dispersion polymerization in the presence of dodecane at various weight ratios of methanol/water media: a 80/20; b 82/18; c 84/16; d 86/14; e 88/12; f 90/10. (Reprinted with kind permission from Springer Science and Business Media from Ref. 84.)

(LMA) was recently applied in the preparation of composite particles by seeded dispersion polymerization with spherical poly(styrene) seed particles.[84] Interestingly, the morphology of the resulting composite particles obtained in the presence of dodecane (a good solvent for LMA) could be tuned by the water/methanol ratio of the emulsion polymerizations. Fig. 15 displays the obtained particle morphologies, changing from golf ball like to spherical, depending on the methanol/water ratio used.[84] A similar change in particle morphology could be obtained by changing the oil droplets from hexane (*via* octane, decane, dodecane, and tetradecane) to hexadecane and these investigations might contribute to the understanding of the formation mechanism of disc-like particles as argued by the autors.[84] Moreover, fatty-acid hydroperoxides were applied as initiators for the mini-emulsion polymerization of acrylates revealing that the chemical composition of the hybrid latexes can be varied ranging from an alkyd fraction of 25% to an alkyd fraction of 75%. Particles without intraparticle heterogeneity were obtained and, compared to a blend system, the alkydacrylic hybrid latexes revealed faster drying, increased hardness and resulted in clear films over a wider composition range.[85,86]

Moreover, oleic acid was applied as end-capper for the one-pot synthesis of oleic acid end-capped temperature-sensitive amphiphilic random poly(*N*-isopropylacrylamide-*co*-*N*,*N*-dimethylacrylamide) introducing also interesting pH-sensitivity to the obtained polymer making it a potential candidate for controlled release applications.[87]

Other approaches (ADMET, olefin polymerization, ring opening polymerization)

Another promising approach to obtain high molecular weight polymers from plant oils renewable resources is the application of acyclic diene metathesis (ADMET) polymerization as has already been shown in the literature.[88,89] Metathesis in general is a successful approach to derivatise the double bonds present in unsaturated fatty acid derivatives in order to obtain new polymerizable monomers.[90] It has been shown that the metathetical ethenolysis of the main fatty acid esters from meadowfoam oil yields a variety of polymerizable compounds (Fig. 16).[90] For more detailed information about the possibilities of self- and cross-metathesis with heterogeneous as well as homogeneous catalyst systems in oleochemistry, the reader is referred to a recent review article.[91]

The obtained terminally unsaturated C_6 methyl ester could be used for the preparation of the corresponding epoxide as well as several dicarboxylic acid derivatives.[90] All obtained monomers were polymerized by a variety of different techniques, including insertion-type copolymerization of terminal olefins with ethylene ($M_w \sim 85$ kDa; $T_g \sim -50$ °C; amorphous), ring-opening polymerization of 5-epoxy hexanoic acid ($M_w > 200$ kDa) and polycondensation of the dicabroxylic acid derivatives with diols ($M_w = 18$–20 kDa; $T_m > 50$ °C).[90] Additionally, ADMET polymerizations of fatty acid
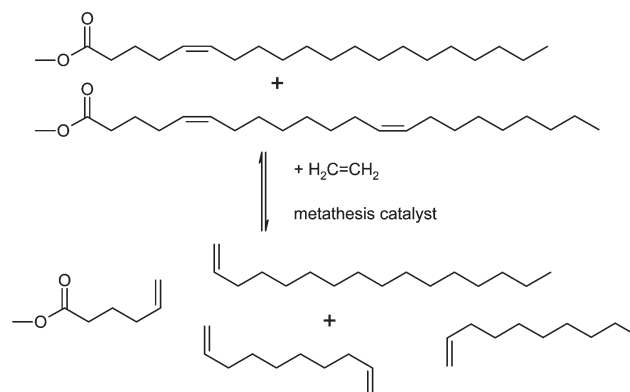

Fig. 16 Metathesis of the main fatty acid esters from meadowfoam oil.[90]

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derived α,ω-alkylene dialkenoates were performed to obtain products with molecular weights up to 100 kDa (Fig. 17).[88]

Interestingly, in 2005 Materia Inc. and Cargill announced a partnership to develop processes for converting biobased oils to industrial chemicals, feedstocks and consumer products.[92] According to information from Materia Inc., significant progress has been made in the ethenolysis process of fatty acid derivatives due to the development of more efficient metathesis catalysts boosting turnover numbers (TON) of soybased biodiesel to 200,000 recently.[93]

Controlled synthesis

The control of polymer architecture, molecular weight, end-group and other parameters with the aim of generating defined chemical, physical and biological properties of the studied materials is of major interest in current polymer science. Living anionic polymerization, discovered by Michael Szwarc,[94] was the first polymerization technique that allowed the above mentioned precise synthesis of defined macromolecules. Today, a variety of living and controlled polymerization techniques are available,[95–101] which have in common the effort to diminish unwanted side reactions, such as irreversible chain transfer or chain termination. By definition, a living polymerization follows a chain growth mechanism with the absence of chain termination and chain transfer processes resulting in most cases in a constant number of growing chains, if the rate of chain initiation (k_i) is fast compared to the rate of chain propagation (k_p)[102] (generally, a ratio of $k_i/k_p >$ 10 is required in order to obtain polymers with a narrow molecular weight distribution).[103]

To our surprise, very little is reported in the literature concerning living or controlled polymerization techniques of plant oil derived monomers. Up to now only a few examples of, atom transfer radical polymerization (ATRP), cationic ring opening polymerization (CROP), group transfer polymerization (GTP) as well as living anionic polymerization of plant oil derived monomers has been described in the literature. The anionic polymerization of lauryl methacrylate (LMA) at -40 °C in THF in the presence of additives (e.g. dilithium salt of triethylene glycol, LiCl, or LiClO$_4$) resulted in polymers with a narrow molecular weight distribution, when optimized conditions were applied (PDI < 1.10).[104] Moreover, diblock copolymers of methyl methacrylate (MMA) and LMA with narrow molecular weight distribution could be synthesized by this technique by sequential addition of monomers. As a justification of these investigation it was mentioned that block copolymers containing inner PLMA soft segments ($T_g =$ -65 °C) and outer PMMA hard segments ($T_g = 110$ °C) could show improved properties as a new class of thermoplastic elastomers.[104] Prior investigations of the living anionic polymerization of long chain methacrylates failed and resulted in broad polydispersity indices or low reaction rates, most
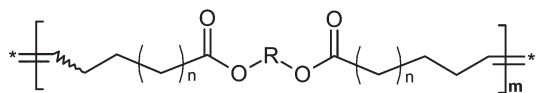

Fig. 17 Plant oil derived polyesters obtained by ADMET polymerization.[88]

likely due a low solubility of these monomers in THF and toluene at -78 °C.[105,106] Moreover, fatty alcohols are industrially applied for the synthesis of ethoxylated surfactants by the controlled anionic polymerization of ethylene oxide. The synthesis of PMMA–b–PLMA diblock copolymers using GTP was already described in 1987.[107] However, only low molecular weight polymers ($M_n = 6500$ g mol^{-1}) with a narrow molecular weight distribution (PDI = 1.14) were obtained. Later, GTP could be applied to prepare narrowly distributed random and diblock copolymers of MMA and LMA with molecular weights up to about 40 kDa (PDI = 1.15) in THF at room temperature.[108] Moreover, the co-polymerization of ethylene with unsaturated fatty acid methyl esters with chain length of C$_6$, C$_7$, C$_{10}$, C$_{11}$ and C$_{14}$ using a cationic palladium catalyst was investigated.[109] The monomers were prepared by metathetical cleavage of plant oil derived fatty acids as discussed above. Branched functionalized polyolefins were thus obtained with molecular weights up to 85 kDa (M_w; PDI = 1.19). These polymers exhibited viscoelastic properties with T_g values of -65 to -55 °C. The most frequently reported controlled polymerization technique applying fatty acid derived monomers seems to be ATRP, whereas other controlled radical polymerization techniques, such as nitroxide mediated polymerization (NMP) or reversible addition–fragmentation chain transfer (RAFT) polymerization, to the best of our knowledge, have not yet been applied to such monomers. For instance, a study of a variety of ligands in the polymerization of LMA by ATRP revealed that N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) and N-(n-propyl)-2-pyridylmethanimine (PPMI) yielded moderate results with regards to the control over the polymerization, whereas bipyridyl based ligands could not adequately control the polymerization.[110] Moreover, controlled polymerization of higher alkyl methacrylates, e.g. LMA and stearyl methacrylate (SMA), has been successfully achieved by bulk ATRP at ambient temperature using CuCl/PMDETA/tricaprylylmethylammonium chloride (Aliquatw336) as the catalyst system and ethyl 2-bromoisobutyrate as the initiator.[111] However, improved control was achieved if THF was added to the system. The effectiveness of the studied catalyst system could be demonstrated by the synthesis of several narrowly distributed block copolymers (e.g. PSMA–b–P^{t}BMA, PMMA–b–PLMA–b–PMMA, and PnBMA–b–PMMA–b–PLMA–b–PMMA–b–PnBMA) at 35 °C (see Fig. 18 for an example).[111] Furthermore, the ATRP of LMA in different solvents with ethyl-2-bromobutyrate as initiator and CuCl/PMDETA as the catalysts has been investigated.[112] The rate of polymerization followed first order kinetics with respect to the monomer and was faster in N,N-dimethylformamide than in other solvents (acetonitrile, anisole, benzene, or toluene). In addition, the molecular weight distributions in anisole and acetonitrile were a little narrower than those obtained when the polymerization was performed in the other investigated solvents.[112] Moreover, reverse ATRP of SMA using 2,2′-azobisisobutyronitrile as the initiator was studied revealing a linear molecular weight increase with conversion, rather narrow molecular weight distributions and first-order kinetics with respect to the monomer.[113] Molecular weights up to 150 kDa (PDI = 1.36) could be achieved with this technique.

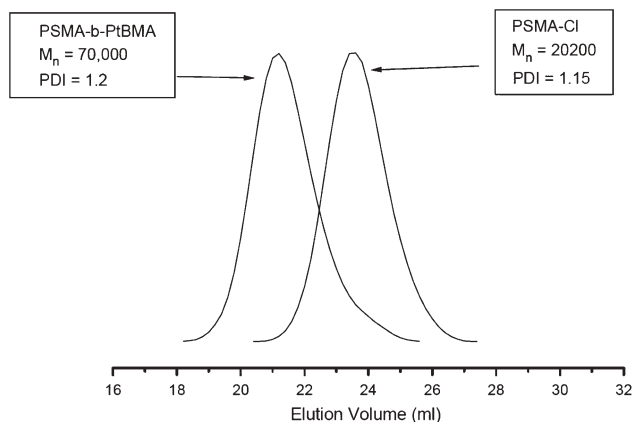|								
16	18	20	22	24	26	28	30	32

Elution Volume (ml)

Fig. 18 Size exclusion chromatography traces of a poly(stearyl methacylate)–Cl macroinitiator and the resulting poly(stearyl methacylate)–*b*-poly(*tert*-butyl methacylate) diblock copolymer. (Reprinted with permission from Ref. 111, Copyright (2006), Elsevier.)

Last but not least the cationic ring-opening polymerization (CROP) of a soy-based 2-oxazoline monomer (SoyOx) was performed in a living fashion under microwave irradiation.[114] The living CROP of bulk SoyOx reached full conversion within eight minutes and the double bonds of the fatty acids side chains were unaffected by the applied polymerization procedure. It could be demonstrated that the unsaturated side chains can be cross-linked and that block copolymers of this monomer can be used to prepare core cross-linked micelles that show unusual morphological features, such as a change from spherical to rice grain like morphology, when changing the solvent from water to acetone.[115] Summarizing the controlled and living polymerizations studied so far with plant oil derived monomers, it can be concluded that very little is known about either their polymerization behavior or their block copolymer properties. Basically only lauryl methacrylate (LMA) and stearyl methacrylate (SMA) have been studied and all other chain lengths have been neglected; only one example of a polymer with narrow polydispersity index bearing a natural fatty acid distribution has been described in detail. However, not only will these materials come into focus when fossil oil reserves are depleted, but they bear manifold possibilities for detailed studies of structure–property relationships of the obtained tailor made (co)-polymers.

Contribution of plant oil renewable resources to a sustainable development

Agenda 21 calls for "criteria and methodologies for the assessment of environmental impacts and resource requirements throughout the full life cycle of products and processes" (Chapter 4.20), and in numerous chapters it discusses the aims and measures necessary for chemistry to make significant contributions. These aims and measures have to be considered for an assessment of chemical processes and products with regards to their contribution to a sustainable development. Generally, the contribution of a specific product to a sustainable development can be considered as manifold:

— The stress on the environment and consequently on the population by chemical production and its emissions as well as the chemical substances that are emitted into the environment for useful purposes that also have negative side effects.[116]

— The more efficient exploitation of the resources in order to create conditions so that in 2050 nine billion people can live in human dignity on earth.

Glycerol

Glycerol, as a by-product of biodiesel production, is an important factor when considering the sustainability of plant oil derived chemicals. Biodiesel production in the EU added up to 3.2×10^6 tonnes in 2005, showing a steady increase.[117] The production of fatty acids and esters (biodiesel) from triglycerides gives about 10 wt% of glycerol. Therefore, glycerol is currently discussed as a platform chemical of a future biobased chemical industry.[118] The production of propylene glycol from glycerol was recently announced by Dow, who call the new product propylene glycol renewable.[119] Moreover, Huntsman Corp. is exploring similar options and Cargill–Ashland and Archer Daniels Midland are planning to produce propylene glycol from glycerol.[119] Cargill–Ashland is starting this business-line with a 65,000 tonnes per annum plant in Europe.[120] Moreover, Dow and Solvay have decided to build plants for the production of epichlorohydrin from glycerol rather than from allyl chloride.[119] Furthermore, 1,3-propanediol can be produced from glycerol using biotechnological methods.[121] As is commonly known, propylene glycol as well as 1,3-propanediol and epichlorohydrin are important industrial monomers that up to now are petrochemical raw materials. Therefore, the described approaches can provide a straightforward contribution to a sustainable development.

Approaches to the assessment of the sustainability of chemical processes

The process parameters of established processes are (at least internally in companies) known and can be used for the quantification of the use of resources, gross energy requirements (GER), waste, emissions, and related costs per product unit. A number of metrics have been developed which are used for such evaluations in the chemical industry.[122–125] Further criteria such as waste, investments, expected profit, and social acceptance need to be included to enable a sound decision.

The GER is accessible for a number of processes carried out at the moment to produce important organic base chemicals and intermediates:[1,126] for example, it is approximately 40 GJ per tonne for acetaldehyde, 80 GJ per tonne for adipic acid, and 104 GJ per tonne for propylene oxide; vegetable oils such as rape seed oil and linseed oil require a GER of approximately 20 GJ per tonne.[127] The difference in the resource consumption depending on the source is so significant that it can be assumed that products based on vegetable oils could clearly be more environmentally benign than petrochemical products. Significantly different values for the GER are also evident in important bulk plastics. For example, the GER for epoxy resin is 107 GJ per tonne, which is almost twice as high as it is for alkyd resins at 64 GJ per tonne due to the fact that the latter contains a portion of renewable raw material, *i.e.*

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plant oil.[128] These examples show that the GER, in relation to the process energy and the chemical energy accumulated in the product, is a useful measure for the assessment of bulk products.

Life-cycle assessment (LCA)

A life-cycle assessment[129] of a product is drawn from the "cradle to the grave", that is, from the extraction of raw materials to waste disposal or recycling. A life-cycle assessment consists of a goal and scope definition, inventory analysis, impact assessment, and interpretation. These proceedings are described in the ISO EN DIN 14040-43[130] and life-cycle assessments were thus set up for bulk plastics.[131] Patel *et al.* recently reviewed LCAs of bio-based polymers and natural fibres.[132] A comparison of energy and greenhouse gas savings by bio-based polymers relative to their petrochemical counterparts revealed, with two exceptions, important advantages for the renewables for the 12 considered examples. Moreover, leading surfactant and detergent producers compared the production of fat alcohol sulfate on the basis of renewable raw materials with the petrochemical production in a life-cycle assessment.[133] It was stated that resource and energy consumption as well as emissions for the surfactant based on palm oil were clearly more favourable than for the one being produced from fossil feedstock. The LCAs of various plant oils are available for soy bean oil,[134] palm oil,[135] and used vegetable oils[136] and comparative LCAs were performed on coolants based on native fat ester.[137] Moreover, the comparison of UV-curable coatings, with linseed oil epoxide as a binder, to a binder produced on a petrochemical basis was shown to have clear advantages for the renewable raw material linseed oil.[127,132] The gross energy requirements as well as the CO_2 and NO_x emissions were shown to be almost one order of magnitude smaller when linseed oil epoxide was used. It is worth noting that the production of the petrochemically derived binder, propylene oxide, contributes more than half of the environmental impact. More than 4 million tonnes per annum of propylene oxide are produced globally, being used mostly for the production of polyetherpolyoles (approx. 80%) for polyurethanes and of propylene glycol (20%) for polyesters.[138] Also this example clearly demonstrates that the substitution of products derived from propylene oxide by products derived from fats and oils will have an important contribution to a sustainable development.

Summary and outlook

Plant oils as well as fatty acid derivatives have been used in polymer science for a long period of time. These renewable resources have proved to be a useful basis for the synthesis of a variety of monomers as well as linear and cross-linked polymers of different types (*e.g.* polyolefns, polyesters, polyethers, polyamides, epoxy and polyurethane resins, and others). Within this contribution we discussed their use for the synthesis of cross-linked as well as linear polymers. The material properties as well as molecular characteristics of the obtained polymers were discussed and compared showing that the application possibilities of these raw materials are manifold. Moreover, knowledge gaps were identified and

possible further developments discussed. In our opinion, especially the study of well defined polymers for specialty applications, obtained by controlled/living polymerization techniques, will improve the application possibilities as well as the scientific knowledge of fatty acid based monomers and polymers. Finally, sustainability contemplations revealed advantages for renewable raw materials by considering gross energy requirements as well as life-cycle assessments.

In summary, the discussed, recent developments highlighted within this contribution clearly show that there is still a large potential for interesting new monomers, polymeric materials as well as model systems in all described areas of research.

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