Aliphatic Long-Chain C₂₀ Polyesters from Olefin Metathesis

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Self-metathesis of undecenoic acid with [(PCy₃)₂Cl₂Ru=CHPh] (**2**), followed by exhaustive hydrogenation yielded pure 1,20-eicosanedioic acid (**5**) (>99%) free of side-products from isomerization. Polycondensation with eicosane-1,20-diol (**6**), formed by reduction of the diol, yielded polyester 20,20 (*T_m* = 108 °C). By comparison, the known ADMET polymerization of undec-10-enyl undec-10-enoate (**7**), and subsequent exhaustive polymer-analogous hydrogenation yielded a polyester (poly-**8**) with irregular structure of the ester groups in the polymer chain (–O(C=O)– vs. –C(=O)O–) (*T_m* = 103 °C). Hydrogenation of secondary dispersions of poly-**7** yielded aqueous dispersions of the long-chain aliphatic polyester poly-**8**.

Introduction

Today's applications of polyesters are dominated by materials based on aromatic diacids, most prominently polycondensates of terephthalic acid with C₂ to C₄ linear diols. While obviously the application-relevant property profile of any polymeric materials depends on numerous properties, one significant disadvantage of aliphatic polyesters are their lower melting points.^[1] Apart from the very short-chain aliphatic polyesters, melting points of polyesters based on common aliphatic monomers are too low for thermoplastic processing. An increased interest in the utilization of renewable feedstocks, and on a different level also biodegradability, enhances the urgency of this issue.^[2,3]

Short-chain aliphatic polyesters based on renewable resources, namely poly(lactic acid) and poly(hydroxy

butyrate)s, have been launched more recently on a large scale. They are produced from carbohydrate feedstocks. In view of the aforementioned challenge, fatty acids from plant oils^[4,5] are attractive substrates as they contain long chain linear segments which can provide crystallinity. The most common fatty acids in plant oils are C₁₆ and C₁₈ compounds. Segments of this chain length in polyesters already provide significant crystallinity, and enhanced melting and crystallization points. This requires an incorporation of these hydrocarbon chains into α,ω -difunctional linear monomers. A possible approach is enzymatic ω -oxidation of saturated fatty acids.^[6] Issues of interest are increased space-time yields, and catalytically active microorganisms which can be nurtured by feedstocks less costly than glucose. By modification of yeast strains, the C₁₄ ω -hydroxy fatty acid can also be obtained selectively.^[7] An entirely chemical route is represented by isomerizing alkoxycarbonylation^[8] of unsaturated fatty acids.^[9] Polymerization grade purity C₁₉ and C₂₃ α,ω -dicarboxylic acid esters were generated from methyl oleate and ethyl erucate, respectively.^[10] While this reaction incorporates the fatty acid completely and without breaking C–C bonds, metathesis reactions can also yield long chain α,ω -dicarboxylic acid esters by coupling of two =CH(CH₂)_{*n*}COOR fragments, followed by hydrogenation to

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the saturated product. These fragments can be generated either by self-metathesis of unsaturated fatty acids $RCH=CH(CH_2)_nCOOR$,^[11] or from other compounds $R'CH=CH(CH_2)_mCOOR$ ($R'=H$, alkyl) generated from fatty acids.^[12] Note that if a single pure starting material is employed in order to form a uniform product and in the absence of isomerization, this will afford even carbon number dicarboxylic acids. One approach to such a starting material is pyrolysis of ricinoleic acid to undecenoic acid ($R'=H$, $n=8$) and heptanal.^[13] We report here aliphatic polyesters generated via metathesis of undecenoic acid and its derivatives.

Results and Discussion

Monomer Synthesis

Isomerization as a potential side-reaction of self-metathesis of an ω -functionalized 1-olefin substrate will ultimately result in the formation of shorter chain α,ω -difunctional products, due to metathesis of internal olefins generated from the substrate. Moreover, secondary metathesis of isomerization products of the desired self-metathesis product can provide further compounds with different chain-lengths. To avoid the formation of these variable chain length compounds, self-metathesis of undecenoic acid (**1**) with $[(PCy_3)_2Cl_2Ru=CHPh]$ (**2**, Grubbs 1st generation catalyst) was employed (Scheme 1). Albeit **2** is less reactive and less tolerant of polar and protic functionalities by comparison to its N-heterocyclic carbene analogue $[(PCy_3)(\eta-C_3H_4N_2Mes_2)Cl_2Ru=CHPh]$ (**3**, Grubbs 2nd generation catalyst), it disfavors olefin isomerization.^[14–17] Isomerization is also reduced in the presence of carboxylic acid groups, present in the substrate in the case studied here.^[18,19] This procedure provided the desired C_{20} diacid **4** in pure form (>99%) after workup, as illustrated by gas chromatographic analysis (Figure 1) after hydrogenation to the desired monomer 1,20-eicosanedioic acid (**5**). As expected, hydrogenation of **4** to **5** with Pd on charcoal under standard conditions (50 bar H_2) was complete within the experimental limit of detection (>99.9% degree of hydrogenation). By comparison, in the self-metathesis product of the corresponding carboxylic acid ester, ethyl undecenoate, obtained under similar conditions, the

Figure 1. Gas chromatogram of 1,20-eicosanedioic acid (**5**), esterified with methanol for analysis (5% diphenyl–95% dimethyl polysiloxane column; 90 °C isothermal for 1 min, 30 K · min^{−1} to 280 °C, isothermal for 8 min).

shorter C_{19} diacid formed from isomerization products was also detected.

The aforementioned advantages of the self-metathesis of undecenoic acid were also exploited for the preparation of the C_{20} diol. Thus, 1,20-eicosanediol (**6**)^[20] was generated by reduction of **5**. For comparison, self-metathesis of undec-10-en-1-ol under similar conditions as employed for the preparation of **4** indeed afforded observable side products formed via isomerization.

A corresponding α,ω -diene (**7**) for ADMET polymerization was prepared by esterification of undecenoic acid (**1**) with undec-10-en-1-ol catalyzed by titanium isopropoxide as previously reported by Meier and coworker.^[21] Gas chromatographic analysis of **7** revealed a purity of 99% (Figure S1).

Polyesters

Polycondensation of stoichiometric amounts of 1,20-eicosanedioic acid (**5**) and eicosane-1,20-diol (**6**) catalyzed by titanium alkoxides in the melt under optimized conditions (temperature and vacuum protocol, and catalyst loading) yielded poly[1,20-eicosadiyl-1,20-eicosanedioate] with a molecular weight of $\bar{M}_n$ 10⁴ g · mol^{−1} as determined by analy-

Scheme 1. Synthesis of monomers for polyesterification (**5** and **6**), and ADMET monomer **7**.

sis of endgroups ($-\text{COOH}$ and $-\text{CH}_2\text{OH}$, and catalyst-derived $-\text{COOR}$) from ^1H NMR spectra (acquired at 130°C in tetrachloroethane- d_2). The material melts with a peak temperature of $T_m = 108^\circ\text{C}$ and crystallizes at $T_c = 83^\circ\text{C}$, with an enthalpy of $\Delta H_m = 151 \text{ J} \cdot \text{g}^{-1}$ (Figure S5). Wide angle X-ray scattering yields a degree of crystallinity χ of about 68%. This data corresponds to an enthalpy of fusion of the crystalline portion of ca. $\Delta H_u = 222 \text{ J} \cdot \text{g}^{-1}$. By comparison to shorter chain aliphatic polyesters, e.g. poly(decamethylene sebacate) $\Delta H_u = 148 \text{ J} \cdot \text{g}^{-1}$,^[1b] this higher value of the melt enthalpy per mass unit reflects the increasing hydrocarbon character of the long-chain polyester, and agrees with the properties of other long-chain polyesters.^[10]

For comparison, a polyester was generated by ADMET of the α,ω -diene **7** similar to a previously reported procedure.^[21] Polymerization by **2** as a catalyst precursor in vacuum (0.025 mbar) for two days yielded poly-**7** with an apparent molecular weight of $\bar{M}_n = 2.8 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ ($\bar{M}_w/\bar{M}_n = 1.9$) as determined by GPC versus polystyrene standards in THF (Figure S2). Reduction of the double bonds of poly-**7** with Pd on charcoal under hydrogen pressure proceeded completely within experimental error ($>99.9\%$) to the fully saturated polyester poly-**8**, as evidenced by the absence of olefinic proton resonances in ^1H NMR spectra (Figure 2). From the resonances of the alkyl endgroups at δ 0.86 ppm a molecular weight of $\bar{M}_n 10^4 \text{ g} \cdot \text{mol}^{-1}$ was determined. This is in reasonable agreement with the apparent molecular weight from GPC of the unsaturated precursor polymer poly-**7**, indicating that no excessive formation of cycles has occurred. Interestingly, in the NMR spectra of poly-**7** in addition to the expected vinyl endgroups (multiplets at 5.79 and 4.95 ppm) saturated

endgroups (triplet at 0.86 ppm) which result from isomerization of terminal vinyl groups are observed.

Poly-**8** features a peak melt temperature of $T_m = 103^\circ\text{C}$ and a crystallization temperature of $T_c = 88^\circ\text{C}$, with $\Delta H_m = 178 \text{ J} \cdot \text{g}^{-1}$ (Figure S4). By comparison, the unsaturated precursor polymer poly-**7** with double bonds in the main chain possesses a lower melt temperature and crystallinity as expected ($T_m = 60^\circ\text{C}$, $T_c = 45^\circ\text{C}$, $\Delta H_m = 127 \text{ J} \cdot \text{g}^{-1}$) (Figure S3).

By comparison to poly[1,20-eicosadiyl-1,20-eicosanedioate], the melting point of poly-**8** is slightly lower. Given that the molecular weights of both materials are similar, and that molecular weights are in a regime sufficiently high for melting points to be little dependent on molecular weight,^[1] this appears to be a minor factor. In the polymer generated via ADMET the ester groups will be oriented in a random fashion, that is in addition to segments $-\text{O}(\text{CH}_2)_{20}\text{O}-$ and $-\text{C}(=\text{O})(\text{CH}_2)_{18}\text{C}(=\text{O})-$ also $-\text{O}(\text{CH}_2)_{19}\text{C}(=\text{O})-$ will occur. This irregularity can contribute to lower melting points. A contribution may also result from isomerization as a side reaction of ADMET, which will result in variable length methylene sequences in the polymer. On a polymer specifically designed towards this issue containing post-polymerization cleavable groups to enable GC-MS analysis, Meier et al. demonstrated that indeed isomerization is a relevant side reaction of ADMET with the N-heterocyclic carbene substituted ruthenium alkylidene **3**, which is more prone to isomerization than catalyst precursor **2** used in this work.^[22]

Aqueous polymer dispersions are produced on a large scale. They are employed for a variety of applications, such as environmentally benign coatings and paints.^[23]

■ Figure 2. ^1H NMR spectra (25°C , CDCl_3) of unsaturated polyester poly-**7** from ADMET (top) and saturated polyester poly-**8** (bottom).

Figure 3. TEM micrograph of a dispersion of saturated polyester (poly-8).

The lower melting point and crystallinity, and related higher solubility in organic solvents of the unsaturated polyester (poly-7) by comparison to its saturated analogue can be beneficial for the generation of aqueous dispersions of long chain aliphatic polyesters. In preliminary studies, an aqueous dispersion was generated by emulsification of a toluene solution of the unsaturated polyester in an aqueous surfactant solution by means of ultrasonication. Catalytic hydrogenation (80 bar H_2 and 60 °C) of this dispersion with Wilkinsons catalyst was complete as evidenced by the absence of olefinic resonances in 1H NMR spectra of isolated bulk material (corresponding to a degree of hydrogenation of >99.9%). Average particles sizes of the dispersions as determined by DLS were around 35 nm, the size was not altered significantly during the hydrogenation procedure (Figure S6). These particle sizes are in qualitative agreement with transmission electron microscopy studies (Figure 3).

Conclusion

Self-metathesis of fatty acid derived ω -functionalized 1-olefins under appropriate conditions in combination with exhaustive hydrogenation yields pure even carbon number α,ω -diacids, as studied here for the preparation of 1,20-eicosanedioic acid from undec-10-enoic acid. Polycondensation with eicosane-1,20-diol, obtained from the diacid via reduction, yields polyester 20,20. By comparison, an aliphatic polyester generated by a reverse sequence of esterification and subsequent metathesis polymerization (ADMET) possessed a lower melting point, which may be related to its irregular structure with regard to the incorporation of the ester groups in the polymer chain, $-O(C=O)-$ versus $-C(=O)O-$, and to the occurrence of variable length methylene segments from isomerization under the conditions employed for the polymerization step.

Aqueous dispersions of aliphatic polyesters can be generated via secondary dispersion of an unsaturated polyester and hydrogenation in dispersion.

Acknowledgements: We thank Marina Krumova for TEM analysis, Lars Bolk for GPC studies and Elana Harbalik for WAXS measurements.

Keywords: dispersions; metathesis; polyesters; thermal properties; thermoplastics

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