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Long-Chain Linear C_{19} and C_{23} Monomers and Polycondensates from Unsaturated Fatty Acid Esters

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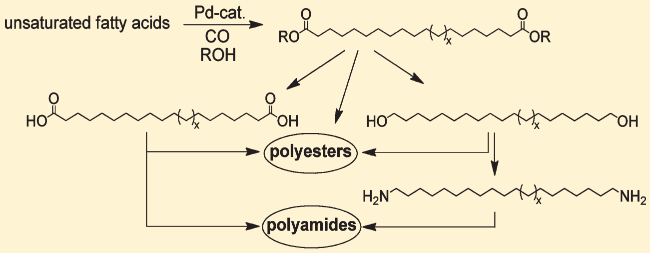
S *Supporting Information*

ABSTRACT: Isomerizing alkoxycarbonylation of methyl oleate and ethyl erucate, respectively, yielded dimethyl 1,19-nonadecanedioate and diethyl 1,23-tricosanedioate in >99% purity. With [κ^2-($\hat{P}$P)Pd(OTf)][OTf] as a defined catalyst precursor ($\hat{P}$P = 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene) the reaction can be carried out without the need for additional added diphosphine. Saponification of the diesters yielded 1,19-nonadecanedicarboxylic acid and 1,23-tricosanedicarboxylic acid in >99% purity. By ruthenium-catalyzed reduction of the diesters with H_2, 1,19-nonadecanediole and 1,23-tricosanediole were formed in high yield and purity (>99%). From the latter, 1,19-nonadecanediamine and 1,23-tricosanediamine were generated. Polyesters with commercially available shorter-chain petrochemical or renewable diols exhibit high melting points due to the crystallizable long-chain methylene segments from the dicarboxylic acid component, e.g., poly[1,6-hexadiyl-1,23-tricosanedioate] T_m 92, T_c 75 °C. Thermal properties of novel long-chain polyamides are reported.



INTRODUCTION

Today's polymer production relies almost exclusively on fossil feedstocks. This applies particularly to thermoplastic polymers, which represent the largest type of industrial polymers before thermosets and elastomers. In view of the limited range of fossil feedstocks, polymers prepared from alternative renewable resources are desirable on the long-term.[1,2] Current examples of polymers based on renewable resources are cellulose esters and ethers, and poly(lactic acid) and poly(hydroxy alkanoates), which have been launched more recently on a large scale. Also, sugar cane based polyethylene is now produced industrially. These polymers are all based on carbohydrate feedstocks.

Fatty acids from plant oils are attractive substrates for polymers[3,4] as they contain long chain linear segments. Thus, Nylon-11 has been prepared for nearly fifty years from ricinoleic acid.[5] Likewise, sebacic acid, which is polymerized to Nylon-6,10 but also applied for example in corrosion inhibition, is generated by base-catalyzed cleavage of ricinoleic acid.[6] However, both routes utilize only about half of the fatty acid molecule, and thus only partially incorporate the latter in the polyamide chains (also, they require a hydroxy substituted unsaturated fatty acid, of which ricinoleic acid is the only practically available example). A full linear incorporation of the entire fatty acid chain would be desirable, as this would not only utilize the feedstock most efficiently but also employ the potential of the long-chain linear feedstock to provide crystallizable segments. This is important, as aliphatic polyesters accessible from current diacid and diol monomers, based on petrochemical as well as renewable feedstocks, suffer from low melting points,[7] which make them unsuitable for thermoplastic processing applications. The terminal functionalization of fatty acids, or their derivatives like esters, is a formidable challenge. One possible solution is enzymatic ω-oxidation. Hereby, e.g., stearic acid is converted to 1,18-octadecane dicarboxylic acid.[8] Problems to be solved are limited space−time yields and the need to nurture the catalytically active microorganims with costly glucose. Alternatively, ω-hydroxy fatty acids can be obtained by fermentation with modified yeast strains.[9] We have recently communicated an entirely chemical route for the preparation of α,ω-dicarboxylic acid esters with polymerization grade purity from unsaturated fatty acids.[10] Isomerizing alkoxycarbonylation[11] converts the internal double bond deep in the hydrocarbon chain to a terminal ester group highly selectively, as noted first by Cole-Hamilton et al. for unsaturated fatty acids,[12] to yield linear (odd-carbon number) products. Polyesters prepared from these long-chain dicarboxylic acids by polycondensation with diols generated from the former by reduction, namely poly[1,19-nonadecadiyl-1,19-nonadecanedioate] and poly[1,23-tricosadiyl-1,23-tricosanedioate], possess melting points and crystallization temperatures that compare with typical thermoplastics.

We here give a full account on the synthesis of a range of α,ω-functionalized long chain linear compounds based on isomerizing alkoxycarbonylation of fatty acids, and of novel polycondensates thereof.

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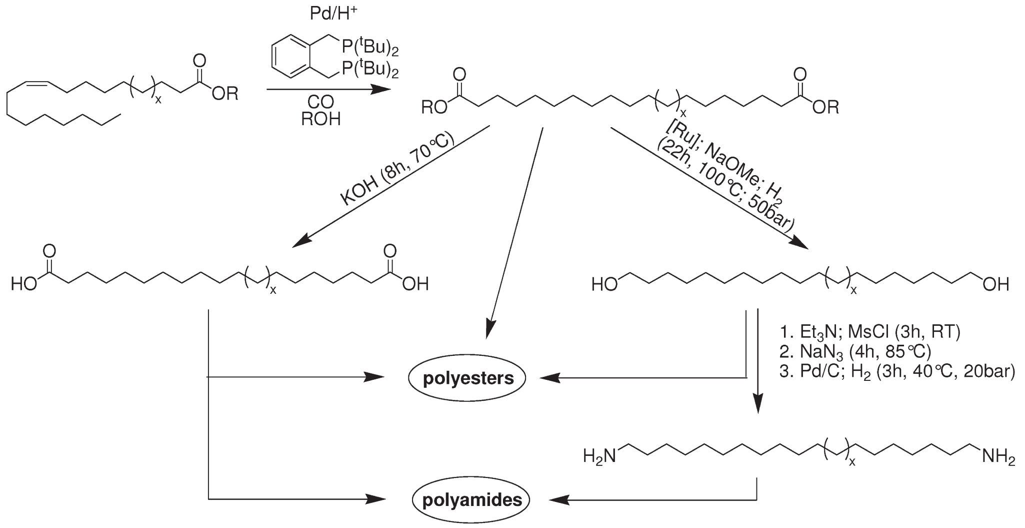
Scheme 1. Long-Chain α,ω-Difunctional Compounds from Unsaturated Fatty Acids ($x = 1$, Oleic Acid as Starting Material; $x = 5$, Erucic Acid)



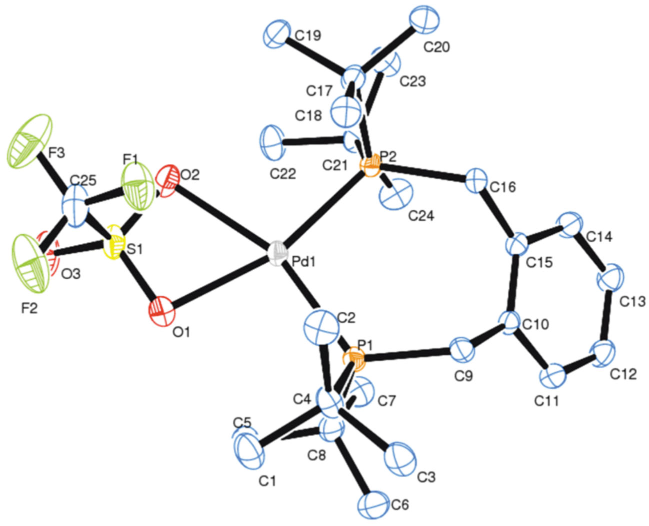


Figure 1. ORTEP plot of $[\kappa^2$-$(\hat{P}P)Pd(OTf)][OTf]$ (**1**). Ellipsoids are shown with 50% probability. Hydrogen atoms, as well as the triflate counterion are omitted for clarity.

■ RESULTS AND DISCUSSION

Beyond their direct utilization as polycondensation monomers, the α,ω-diesters are also of interest for the preparation of other difunctional compounds (Scheme 1). While these conversions principally rely on known chemistry, application to these long-chain compounds in some instances needs to consider that the substrates and the products can differ strongly from lower molecular weight analogues concerning their solubility and physical properties (T_m, T_v) and require suitable reaction and workup conditions.

Isomerizing Alkoxycarbonylation. Previous studies of alkoxycarbonylation of internal olefins employed an in situ catalyst system, consisting of a palladium source mixed with the diphosphine ligand 1,2-bis[(di-*tert*-butylphosphino)methyl]-benzene (dtbpx). The active species formed is very likely $[\kappa^2$-$(\hat{P}P)PdH(L)]$. To achieve reasonable activities, a ca. 5-fold excess of the costly diphosphine[13] was required in the work of Cole-Hamilton[12] as well as in our hands,[10] that is P:Pd = 10:1. While the background for this remains unclear, we reasoned that a defined coordination of the diphosphine in the catalyst precursor might obliviate the need for additional phosphine. A triflate complex was studied as a catalyst precursor, as the relatively weak coordination of triflate should provide a high reactivity. The ditriflate complex $[\kappa^2$-$(\hat{P}P)Pd(OTf)_2]$[14] (**1**) was obtained by halide abstraction from the corresponding dichloro complex $[\kappa^2$-$(\hat{P}P)PdCl_2]$. X-ray diffraction (Figure 1) reveals that only one triflate ligand is coordinated to the metal center, via two of its oxygen atoms, while the second triflate functions as a noncoordinated counterion, that is **1** is best described as $[\kappa^2$-$(\hat{P}P)Pd(OTf)][OTf]$.

Table 1. Isomerizing Methoxycarbonylation of Methyl Oleate with Different Catalyst Systems[a]

entry	catalyst	substrate[d]	% conversion[e]
1	$[\kappa^2$-$(\hat{P}P)Pd(OTf)_2]$[c]	methyl oleate (75%)	36
2	$[\kappa^2$-$(\hat{P}P)Pd(OTf)_2]$[c]	methyl oleate (99%)	80
3	$Pd(OAc)_2$/dtbpx/MSA[b]	methyl oleate (75%)	28
4	$Pd(OAc)_2$/dtbpx/MSA[b]	methyl oleate (99%)	52

[a] Conditions: 12 μmol of Pd, Pd to methyl oleate ratio 1:500, 10 mL of MeOH, 20 bar CO, 90 °C, 22 h. [b] 12 μmol of $Pd(OAc)_2$, 60 μmol of diphosphine, 500 μmol of methanesulfonic acid (MSA). [c] 12 μmol of $[(dtbpx)Pd(OTf)_2]$. [d] Purity of the starting material given in brackets. [e] Conversions, referring to the total mass of the starting material, are calculated from the ^1H NMR spectrum of the crude reaction mixture. Entries 3 and 4 are taken from ref 10.

A remarkably enhanced catalyst performance was observed with this defined catalyst precursor (Table 1). At a palladium to methyl oleate ratio of 1:500, which much exceeds the 1:60 catalyst to substrate ratio employed in previous studies,[10,12] 80% of the fatty acid methyl ester is selectively converted to the α,ω-diester using the ditriflate complex (entry 2), whereas the aforementioned in situ catalyst system with excess phosphine

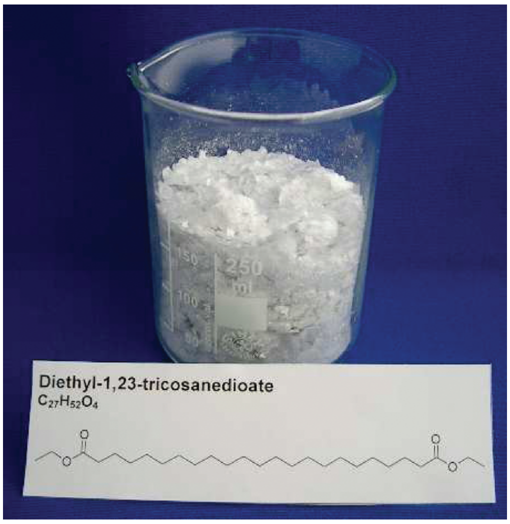


Figure 2. Diethyl 1,23-tricosanedioate from isomerizing ethoxycarbonylation of erucic acid.

only converted 50% (entry 4). Similar results were obtained utilizing readily available technical grade methyl oleate as a starting material (entries 1 and 3).

By comparison to our previous report, in which the α,*ω*-diesters were obtained in amounts of ca. 1.5 g, performing the alkoxycarbonylation on a larger scale in a 300 mL reactor yielded the products in an amount of ca. 25 g per experiment without any adverse effects on purity or yield (Figure 2 and Experimental Section).

α,*ω*-Diols. In our preliminary studies, reduction of the diesters to the diols was achieved by means of the inorganic hydride $LiAlH_4$. While this satisfactorily afforded the products in high purity, removal of the inorganic salts requires a tedious workup, and also on a larger scale the cost of $LiAlH_4$ would be prohibitive. Saudan's ruthenium catalyst, which has been reported[15] to reduce esters with H_2 to alcohols selectively under relatively mild conditions, was found to be suited also for the long-chain substrates subject to this work. Nonadecane-1,19-diol as well as tricosane-1,23-diol both were formed in high yield and with more than 99% purity (from ^1H NMR) via homogeneously catalyzed hydrogenolysis of the corresponding α,*ω*-diesters with dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium at $p(H_2) = 50$ bar and a reaction temperature of 100 °C, employing a high substrate to catalyst ratio of 1000:1. Note that under the reaction conditions the starting material is soluble in the THF solvent employed. Thus, the diols are available in high purity and good yields via a sequence of two effective and selective catalytic reactions from the unsaturated fatty acids, employing only methanol or ethanol, respectively, carbon monoxide, and hydrogen as reagents.

α,*ω*-Dicarboxylic Acids. Carboxylic acids are generally more reactive than their esters. Thus, they can be preferred to the latter for polycondensation reactions. To this end, dimethyl-1,19-nonadecanedioate and diethyl-1,23-tricosanedioate were both hydrolyzed to the corresponding acids using potassium hydroxide in methanol at elevated temperatures ($T = 70$ °C).[16] Recrystallization from toluene affords the long-chain α,*ω*-diacids in more than 99% purity, as revealed by NMR spectroscopy.

α,*ω*-Diamines. Nonadecane-1,19-diamine and tricosane-1,23-diamine were prepared from the corresponding alcohols in three steps: mesylate formation, azide substitution, and catalytic reduction (cf. Scheme 1). The poorly soluble long-chain aliphatic diamines could be both isolated after repeated filtration over a Büchner funnel at 50 °C to remove catalyst residues, and recrystallization from ethanol in an overall yield of about 65%. This three-step synthesis is convenient on a laboratory scale, also due to the relatively high molecular weight per functional group of the long-chain compounds, which limits the amount of tosylate and azide reagent required. On the longer term, routes to the diamines employing lower cost reagents and requiring fewer steps are desirable, such as amidation with ammonia and hydrogenation.

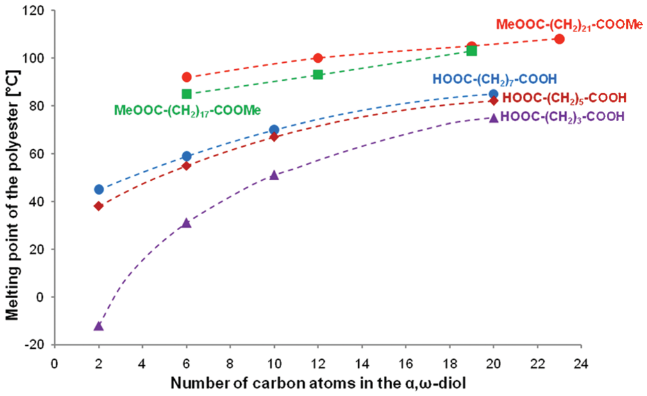


Figure 3. Comparison of the melting points of different polyesters obtained by polycondensation of dimethyl-1,19-nonadecanedioate and diethyl-1,23-tricosanedioate (this work), and of azelaic, pimelic, and glutaric acid (from ref 7a) with α,*ω*-diols of different chain lengths. Dashed lines are merely a guide to the eye.

Polyesters with Variable Chain Length Diols. We have previously communicated the synthesis and properties of the novel polyesters poly[1,19-nonadecadiyl-1,19-nonadecanedioate] and poly[1,23-tricosadiyl-1,23-tricosanedioate], based on the long-chain diacids and diols. These polyesters possess melting points >100 °C and crystallization temperatures around 90 °C, which compares with typical thermoplastics. For aliphatic polycondensates of shorter chain diols, crystallinity should primarily arise from the long-chain diacid component. To this end, the C_{19} and C_{23} diacid, respectively, were condensed with hexane-1,6-diol and with dodecane-1,12-diole, catalyzed by titanium alkoxides. Molecular weights of the resulting polyesters as determined by ^1H NMR spectroscopic analysis of the end groups are around M_n 10^4 g mol^{-1}. All the materials prepared are semicrystalline and thermal analyses reveal melting points from 86 to 100 °C and crystallization temperatures from 72 to 76 °C (Figure 3 and Experimental Section).

By comparison to polycondensates of shorter chain diacids, the melt and crystallization temperatures of the novel polyesters are remarkably enhanced.[7a] Even for the relatively short chain hexanediol the long chain of the diacid component dominates the thermal properties. Accordingly, wide-angle X-ray scattering (WAXS) essentially yields the reflexes of the polyethylene portion of the material. For poly[1,6-hexadiyl-1,19-nonadecanedioate], for example, a degree of crystallinity of about χ 68% was found (Figure 4). These findings point out that high melting and crystallization points, and crystallinity, can be obtained with a large range of shorter chain diols, which can be based on either petrochemical or renewable resources.

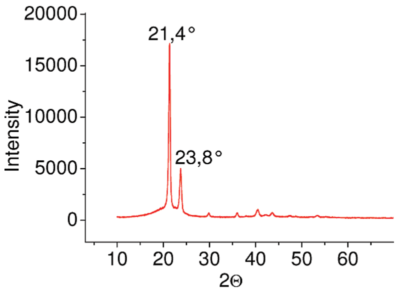


Figure 4. WAXS diffraction pattern of poly[1,6-hexadiyl-1,19-nonadecanedioate].

Polyamides. Polyamides were generated by polycondensation of the novel long-chain α,ω-diamines with the C_{19} and C_{23}, respectively, α,ω-dicarboxylic acids. ^{1}H NMR spectroscopic analyses of end groups on polymer solutions in $C_2D_2Cl_4$ and phenol at 120 °C revealed molecular weights of M_n 10^4 g mol^{-1}. It has been well documented that, due to the prevalence of hydrogen bonding in polyamides, their melting and crystallization temperatures overall tend to decrease with increasing chain lengths of the monomers.[17] Polyamides 23,19 and 23,23, based on 1,23-tricosanediamine, exhibit a T_m 156 °C (T_c 132 °C; ΔH_m 85 J g^{-1}) and T_m 152 °C (T_c 130 °C; ΔH_m 88 J g^{-1}), respectively. For polyamides 11,23 and 12,23, respectively, from polycondensation of the shorter chain 1,11-diaminoundecane or 1,12-diaminododecane with 1,23-tricosanedicarboxylic acid, as expected, higher melting points were found, which amount to T_m 167 °C (T_c 150 °C; ΔH_m 111 J g^{-1}) and T_m 168 °C (T_c 150 °C; ΔH_m 121 J g^{-1}).

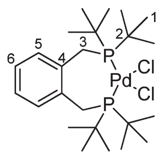
SUMMARY AND CONCLUSIONS

Isomerizing alkoxycarbonylation is a unique reaction in that it converts an internal double bond deep in the alkyl chain of an unsaturated fatty acid into a terminal ester moiety highly selectively. This was applied here to methyl oleate and ethyl erucate as two readily available substrates. The resulting odd carbon-numbered α,ω-diesters were generated on a scale of ca. 25 g per experiment routinely in polycondensation grade purity (>99%), employing a 300 mL laboratory scale pressure reactor. There are no evident limitations to further upscaling of this reaction. These C_{19} and C_{23} α,ω-diesters, which hereby are accessible for the first time in a practicable fashion, provide an entry to a range of novel long-chain α,ω-difunctional compounds. These can serve, among others, as monomers for novel polycondensates. The dicarboxylic acids, as well as the diols were generated in high yield and high purity employing low-cost reagents. The C_{19} and C_{23} α,ω-diamines were prepared in this work in a three-step route. Polyesters with long-chain C_{19} and C_{23} dicarboxylate components exhibit melting points in the general range of thermoplastic materials also with short chain diol components, due to the crystallinity imparted by the dicarboxylate-substituted long-chain methylene segments. Evident issues of future interest are an understanding and further improvement of catalyst performance in the isomerizing alkoxycarbonylation, enhanced polymer molecular weights, and the mechanical and processing properties as well as biodegradation rates of the polycondensates reported here and other materials from these monomers.

EXPERIMENTAL SECTION

Materials and General Considerations. Unless stated otherwise, all manipulations were carried out under inert gas atmosphere using standard Schlenk or glovebox techniques. Methanol and ethanol were distilled from magnesium turnings and iodine. Methylene chloride, dimethylformamide, and pentane were distilled from CaH_2 and stored under argon. Diethyl ether and THF were distilled from sodium/benzophenone under inert conditions. All other solvents were used in technical grade as received. Carbon monoxide (3.7) and hydrogen (5.0) were supplied by Air Liquide. Methyl oleate (99%) was supplied by Sigma Aldrich, technical grade methyl oleate (75%) by ABCR, and ethyl erucate (95%) by TCI. All solvents were degassed by three freeze−pump−thaw cycles prior to use. Methanesulfonic acid (98%), hydrogen chloride solution (2.0 M in diethyl ether), potassium hydroxide (90%), sodium methoxide (95%), triethylamine (99%), methane sulfonyl chloride (≥98%), sodium azide, 1,6-hexanediol (≥99%), 1,12-dodecanediol (99%), and titanium(IV) butoxide (≥97%) were supplied by Sigma Aldrich. Silver triflate (99%) and 1,2-bis(di-*tert*-butyl-phosphinomethyl)benzene (98%) were purchased from ABCR, and palladium/charcoal activated (10% Pd) and palladium(II) chloride from Merck. Bis(dibenzylideneacetone)palladium(0) was purchased from MCAT, Konstanz, Germany, and palladium(II) acetate was from Umicore. All deuterated solvents were supplied by Eurisotop. NMR spectra were recorded on a Varian Inova 400, a Bruker Avance 400 and on a Bruker Avance DRX 600 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-d_2 at 130 °C. For polyamides, phenol (ca. 20 vol %) was added to enhance solubility. DSC analyses were performed on a Netzsch Phoenix 204 F1 instrument with a heating and cooling rate, respectively, of 10 K min^{-1}. Data reported are from second heating cycles.

Dichloro{1,2-bis(di-*tert*-butylphosphinomethyl)benzene}-palladium(II) [(dtbpx)PdCl$_2$].[18,19] Pd(dba)$_2$ (138 mg, 0.24 mmol) was added to a stirred solution of dtbpx (95 mg, 0.24 mmol) in THF (6 mL). After 2 days the orange-red solution was filtered and the solvent removed in vacuo. The resulting orange solid was dissolved in diethyl ether (4 mL), and HCl (0.2 mL of a 2 M solution in diethyl ether) was added to form the desired product as a yellow solid. After stirring for 1 h, the product was filtered off and washed with diethyl ether (3 × 5 mL) and THF (1 × 5 mL). After the product was dissolved in methylene chloride and insoluble solids were filtered off, the desired product was precipitated by slow addition of diethyl ether (93 mg, 68%).



^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 7.45−7.33 (m, 2H, H-6), 7.30−7.18 (m, 2H, H-5), 3.69−3.26 (m, 4H, H-3), 1.61 (d, $^3J_{PH}$ = 14.0, 36H, H-1). ^{31}P NMR (CD_2Cl_2, 25 °C, 162 MHz): δ 36.75 (s). ^{13}C NMR (CD_2Cl_2, 25 °C, 101 MHz): δ 135.49−135.39 (m, C-4), 133.56−133.40 (m, C-5), 127.92 (br s, C-6), 41.70−41.38 (m, C-2), 32.31 (br s, C-1), 30.18−29.96 (m, C-3).

Anal. Calcd. (%) for $C_{24}H_{44}C_{l2}P_2Pd$ (571.88 g mol^{-1}): C 50.41, H 7.76. Found: C 50.76, H 7.58

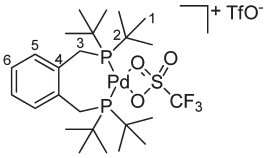
Bis(trifluoromethanesulfonato){1,2-bis(di-*tert*-butylphosphinomethyl)benzene)}palladium(II) [(dtbpx)Pd(OTf)]-[OTf] (1).[14] AgOTf (82 mg, 0.32 mmol) was added to a solution of [(dtbpx)PdCl$_2$] (92 mg, 0.16 mmol) in methylene chloride (6 mL). The orange reaction mixture was stirred overnight at room temperature under the exclusion of light. After the insoluble AgCl was filtered off and

Table 2. Details of the Crystal Structure Determination of 1

formula	$C_{25}H_{44}O_3F_3P_2SPd$, CO_3F_3S
CCDC no.	817578
formula weight, g mol^{-1}	799.07
cryst. size, mm	0.45 × 0.32 × 0.21
space group	*P*21/21/21
a, Å	9.1472(3)
b, Å	11.3899(5)
c, Å	32.6773(10)
α, β, γ deg.	90, 90, 90
V, Å^3	3404.5(2)
Z	4
δ_{calc}, g cm^{-3}	1.559
T, K	100
μ, mm^{-1}	0.831
F(000)	1640
Θ_{max}, deg.	27.96
no. of rflns measd.	43569
no. of unique rflns	8123
no. of rflns $I > 2\sigma(I)$	7865
R_1, $I > 2\sigma(I)$ ^{a}	0.0253
R_1, all data	0.0290
wR_2^{a}	0.0607
diff. Fourier peak min./ max., e Å^{-3}	−0.703/0.581

^{a} $R_1 = \Sigma||F_o - F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

the solvent was removed in vacuo, a dark yellow solid was obtained, which was washed with diethyl ether until the filtrate was clear. The crude product was dissolved in methylene chloride and subsequently precipitated by slow addition of diethyl ether. After removal of solvent residues in vacuo, **1** was obtained as an orange powder (93 mg, 73%). Crystals suited for X-ray diffraction were grown from methylene chloride layered with pentane.



^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 7.48−7.42 (m, 2H, H-6), 7.38−7.32 (m, 2H, H-5), 3.84 (br s, 4H, H-3), 1.58 (d, $^3J_{PH}$ = 15.5 Hz, 36H, H-1). ^{31}P NMR (CD_2Cl_2, 25 °C, 162 MHz): δ 79.12 (s). ^{13}C NMR (CD_2Cl_2, 25 °C, 101 MHz): δ 133.39−133.25 (m, C-4), 131.67−135.51 (m, C-5), 129.11 (br s, C-6), 120.21 (q, $^1J_{CF}$ = 318.3 Hz CF_3), 43.48−43.00 (m, C-2), 31.06 (br s, C-1), 27.1−26.70 (m, C-3). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz): δ −77.62 (s).

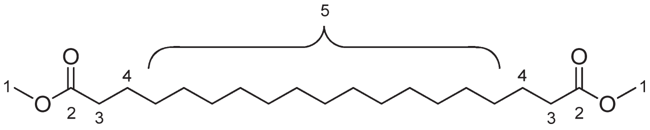
X-ray Diffraction Analysis of Complex 1 : Data are given in Tables 2 and 3. The data collection was performed at 100 K on a STOE IPDS-II diffractometer equipped with a graphite-monochromated radiation source (λ = 0.710 73 Å) and an image plate detection system. A crystal mounted on a fine glass fiber with silicon grease was employed. The selection, integration, and averaging procedure of the measured reflex intensities, the determination of the unit cell dimensions by a least-squares fit of the 2Θ values, data reduction, LP-correction, and space group determination were performed using the X-Area software package delivered with the diffractometer.[20] A semiempirical absorption correction was performed. The structure was solved by Patterson methods (SHELXS-97), completed with difference Fourier syntheses and refined with full-matrix least-squares using SHELXL-97 minimizing $w(F_o^2 - F_c^2)^2$.[21] The Flack-parameter indicated twinning of the crystal. Therefore, a twin law (−1 0 0) (0 0.321 0.330) (0 2.718 −0.331), as determined by the Platon TwinRotMat procedure,[22] was employed by which the BASF parameter refined to 0.001 38. The weighted *R* factor (*wR*) and the goodness of fit *S* are based on F^2; the conventional *R* factor (*R*) is based on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersion factors are provided by the SHELXL-97 program. Hydrogen atoms were treated in a riding model. Thermal ellipsoid representations were created with ORTEP-3.[23] The complete X-ray analysis is deposited as CCDC-817578. Data are given in Tables 2 and 3.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1

Pd1−P1	2.2607(6)
Pd1−P2	2.2808(6)
Pd1−O1	2.2327(18)
Pd1−O2	2.2888(18)
P1−Pd1−P2	99.30(2)
O1−Pd1−O2	62.96(7)
O1−Pd1−P1	96.71(5)
O2−Pd1−P2	101.15(5)

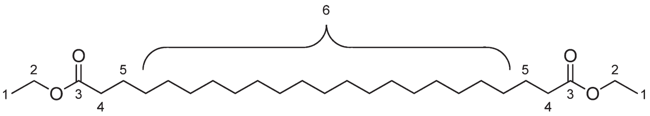
Alkoxycarbonylations. Alkoxycarbonylations of unsaturated long-chain fatty acids esters were carried out in a mechanically stirred 300 mL stainless steel pressure reactor with a glass inlay, equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the reaction mixture. Prior to alkoxycarbonylation experiments the reactor was heated to 30 °C and was then evacuated and purged with nitrogen several times.

Methoxycarbonylation of Methyl Oleate with the in Situ Catalyst System at a Substrate to Catalyst Ratio of 125. $PdCl_2$ (136 mg, 0.768 mmol) was weighed into a Schlenk tube under air, and introduced into a glovebox, where dtbpx (1.5 g, 3.84 mmol) was added. After the Schlenk tube was removed from the glovebox 160 mL of methanol, methyl oleate (32.6 mL of 75% methyl oleate), and methanesulfonic acid (0.5 mL, 7.68 mmol) were added. The reaction mixture was stirred for a few minutes, and then cannula transferred into the pressure reactor. The reactor was closed, pressurized with 20 bar carbon monoxide, and then slowly heated to 90 °C. After 22 h the reactor was cooled to room temperature and vented. The crude product was dissolved in methylene chloride and filtrated over a Buchner funnel to remove solid residues. Removing the solvent in vacuo and recrystallization from methanol yielded dimethyl-1,19-nonadecanedioate (18.1 g, 71%).



^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 3.66 (s, 6H, H-1), 2.30 (t, $^3J_{H-H}$ = 7.6 Hz, 4H, H-3), 1.66−1.58 (m, 4H, H-4), 1.35−1.20 (m, 26H, H-5). ^{13}C NMR ($CDCl_3$, 25 °C, 101 MHz): δ 174.48 (s, C-2), 51.56 (s, C-1), 34.28 (s, C-3), 30.16−29.15 (C-5), 25.12 (s, C-4).

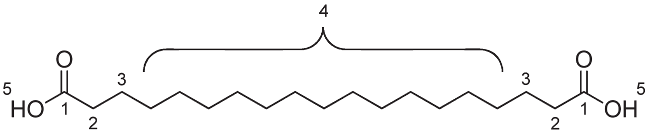
Ethoxycarbonylation of Ethyl Erucate with the in Situ Catalyst System at a Substrate to Catalyst Ratio of 125. $PdCl_2$ (136 mg, 0.768 mmol) was weighed into a Schlenk tube under air and then introduced into a glovebox, where dtbpx (1.5 g, 3.84 mmol) was added. After the Schlenk tube was removed from the glovebox, 160 mL of ethanol, ethyl erucate (40.4 mL of 95% ethyl erucate), and methanesulfonic acid (0.5 mL, 7.68 mmol) were added. The reaction mixture was stirred for a few minutes and then cannula transferred into the pressure reactor. The reactor was closed, pressurized with 20 bar carbon monoxide and then slowly heated to 90 °C. After 22 h the reactor was cooled to room temperature and vented. The crude product was dissolved in methylene chloride and filtrated over a Buchner funnel to remove solid residues. Removing the solvent in vacuo and recrystallization from ethanol yielded diethyl-1,23-tricosanedioate (30.6 g; 76%).



^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz) δ 4.12 (q, $^3J_{H-H}$ = 7.1 Hz, 6H, H-2), 2.28 (t, $^3J_{H-H}$ = 7.6, 4H, H-4), 1.65–1.57 (m, 4H, H-5), 1.3–1.18 (m, 38H, H-1/H-6). ^{13}C NMR (CDCl$_3$, 25 °C, 101 MHz): δ 174.08 (s, C-3), 60.28 (s, C-2), 34.54 (s, C-4), 29.94–29.22 (C-6), 25.14 (s, C-5), 14.40 (s, C-1).

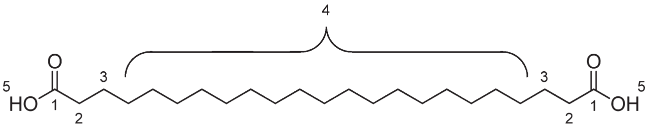
*Alkoxycarbonylation of Methyl Oleate with the Defined Catalyst Precursor [(dtbpx)Pd(OTf)](OTf) (**1**) at a Substrate to Catalyst Ratio of 500.* [(dtbpx)Pd(OTf)](OTf) (**1**) (153 mg, 0.192 mmol) was weighed into a Schlenk tube under an inert atmosphere and dissolved in 160 mL of methanol. Methyl oleate (32.6 mL of 75% methyl oleate) was added. After stirring for a few minutes, the reaction mixture was cannula transferred into the pressure reactor. The reactor was closed, pressurized with 20 bar carbon monoxide and then slowly heated to 90 °C. After 22 h the reactor was cooled to room temperature and vented. The crude product was dissolved in methylene chloride and filtrated over a Buchner funnel to remove solid residues. Removing the solvent in vacuo and recrystallization from methanol yielded dimethyl-1,19-nonadecanedioate (9.0 g, 35%).

Nonadecane-1,19-dicarboxylic Acid. In a round bottomed flask dimethyl-1,19-nonadecanedioate (11.2 mmol, 4.0 g) was suspended in methanol (30 mL) and heated to 70 °C. To this solution was slowly added KOH (70.2 mmol, 4.0 g). The resulting mixture was then refluxed for 2 h during which more methanol (30 mL) was added. After further addition of KOH (62.4 mmol, 3.5 g) the mixture was refluxed for another 8 h. Cooling the suspension to room temperature and removing the solvent in vacuo afforded a white solid, which was suspended in water (60 mL). The suspension was acidified to pH = 2 by adding 3 N hydrochloric acid. The dicarboxylic acid was then filtered off, washed with water, and recrystallized from toluene to give a glittery white solid in 98% yield (3.6 g).



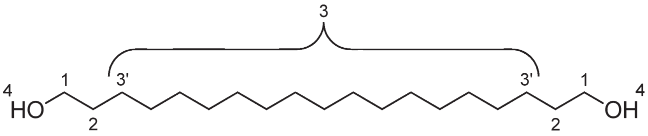
^{1}H NMR (dmso-d_6, 130 °C, 600 MHz): δ 11.19 (br s, 2H, 5-H), 2.19 (t, $^3J_{H-H}$ = 7.3 Hz, 4H, 2-H), 1.58–1.52 (m, 4H, 3-H), 1.35–1.25 (m, 26H, 4-H). ^{13}C NMR (dmso-d_6, 130 °C, 150 MHz): δ 173.22 (C-1), 33.16 (C-2), 28.36–27.83 (C-4), 23.86 (C-3).

Tricosane-1,23-dicarboxylic Acid. Tricosane-1,23-dicarboxylic acid was prepared according to the procedure described above for its shorter chain analogue. Recrystallization from toluene yielded tricosane-1,23-dicarboxylic acid (4.1 g, 96%).



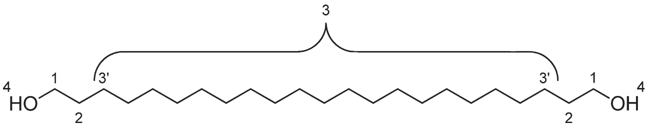
^{1}H NMR (dmso-d_6, 130 °C, 600 MHz): δ 11.34 (br s, 2H, 5-H), 2.41 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, 2-H), 1.59–1.51 (m, 4H, 3-H), 1.36–1.21 (m, 34H, 4-H). ^{13}C NMR (dmso-d_6, 130 °C, 150 MHz): δ 173.18 (C-1), 33.13 (C-2), 28.30–27.82 (C-4), 23.85 (C-3).

Nonadecane-1,19-diol. The reduction was carried out, analogous to a reported procedure,[15] in a 300 mL stainless steel mechanically stirred pressure reactor equipped with a heating jacket and a glass inlay. Prior to the reduction experiment the reactor was purged several times with argon. Dimethyl-1,19-nonadecanedioate (16.8 mmol, 6.0 g) was weighed under air into a dry Schlenk tube equipped with a magnetic stirring bar, which was then purged several times with argon. Dry and degassed THF (40 mL) was added using standard Schlenk techniques. Vigorous stirring afforded a homogeneous reaction mixture. In the glovebox dichlorobis[2-(diphenylphosphino)ethylamine]ruthenium (16.8 μmol, 10 mg) and sodium methanolate (1.10 mmol, 60 mg) were weighed into a second dry Schlenk equipped with a magnetic stirring bar. After the Schlenk tube was removed from the glovebox, 40 mL of dry and degassed THF was added. Both mixtures were then cannula-transferred into the reactor in an argon counter stream. The reactor was closed, pressurized with 50 bar hydrogen and then heated to 100 °C for 22 h. After cooling to room temperature, the reactor was vented. The reaction mixture was retrieved from the reactor and heated to around 50 °C to remove catalyst residues by filtration over a Buchner funnel. Removing the solvent in vacuo and recrystallization from chloroform yielded nonadecane-1,19-diol (4.2 g, 83%).



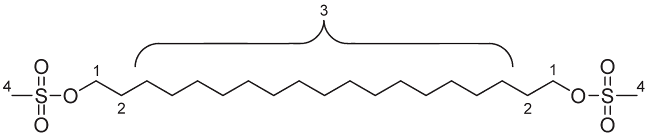
^{1}H NMR (C$_2$D$_2$Cl$_4$, 130 °C, 600 MHz): δ 3.58 (t, $^3J_{H-H}$ = 6.5 Hz, 4H, 1-H), 1.58–1.49 (m, 4H, 2-H), 1.38–1.21 (m, 30H, 3-H), 1.02 (br s, 2H, 4-H). ^{13}C NMR (C$_2$D$_2$Cl$_4$, 130 °C, 150 MHz): δ 63.17 (C-1), 33.15 (C-2), 29.78–29.50 (C-3), 25.99 (C-3′).

Tricosane-1,23-diol. The reduction of diethyl-1,23-tricosanedioate was carried out analogously to the procedure described above for its 1,19-analgoue. After the reaction mixture was retrieved from the reactor, it was heated to around 50 °C and then filtrated over a Buchner funnel to remove catalyst residues. THF was removed in vacuo. Tricosane-1,23-diol was recrystallized from chloroform to obtain 78% yield (4.6 g).



^{1}H NMR (C$_2$D$_2$Cl$_4$, 130 °C, 600 MHz): δ 3.59 (t, $^3J_{H-H}$ = 6.5 Hz, 4H, 1-H), 1.60–1.48 (m, 4H, 2-H), 1.40–1.20 (m, 40H, 3-H), 1.02 (br s, 2H, 4-H). ^{13}C NMR (C$_2$D$_2$Cl$_4$, 130 °C, 150 MHz): δ 63.18 (C-1), 33.15 (C-2), 29.79–29.50 (C-3), 25.99 (C-3′).

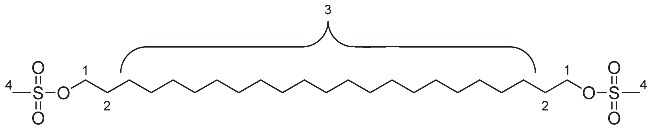
Nonadecane-1,19-dimesylate. In a 100 mL two-necked round bottomed flask nonadecane-1,19-diol (10.0 mmol, 3.0 g) and triethylamine (50 mmol, 5.1 g) were dissolved in THF (40 mL) at 50 °C. To this solution was slowly added mesyl chloride (34 mmol, 3.9 g) via a syringe. The resulting yellow suspension was stirred for 3 h until it turned red. After addition of dichloromethane (150 mL), the reaction mixture was successively washed with water (100 mL), 2 M HCl (100 mL), water (100 mL), saturated NaHCO$_3$ solution (80 mL), and water 100 mL). The organic phase was dried with MgSO$_4$, and the solvent was removed in vacuo. After recrystallization from ethanol, nonadecane-1,19-dimesylate (8.7 mmol, 87%) was obtained as a gleaming white solid.



^{1}H NMR (CDCl$_3$, 25 °C, 400 Hz): δ 4.22 (t, $^3J_{H-H}$ = 6.6 Hz, 4H, 1-H), 2.99 (s, 6H, 4-H), 1.82–1.63 (m, 4H, 2-H), 1.42–1.20 (m, 30H, 4-H).

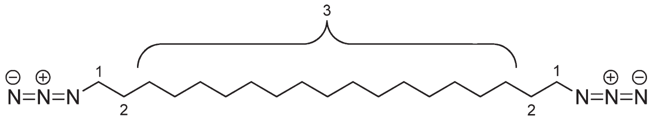
Tricosane-1,23-dimesylate. Tricosane-1,23-dimesylate was prepared analogous to its 1,19-analogue. The organic phase was dried with

$MgSO_4$, and the solvent was removed in vacuo. After recrystallization from ethanol, tricosane-1,23-dimesylate (8.7 mmol, 87%) was obtained as a gleaming white solid.



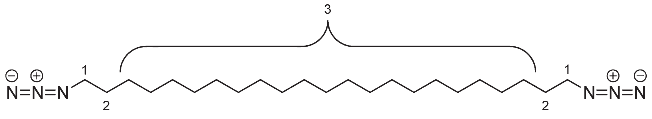
^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 4.22 (t, $^3J_{H-H}$ = 6.6 Hz, 4H, 1-H), 3.00 (s, 6H, 4-H), 1.80−1.69 (m, 4H, 2-H), 1.46−1.18 (m, 38H, 4-H).

Nonadecane-1,19-diazide. In a round bottomed flask nonadecane-1,19-dimesylate (8.0 mmol, 3.7 g) was dissolved in DMF (60 mL) at 65 °C. To this solution was added sodium azide (40 mmol, 2.6 g). The resulting mixture was stirred at 85 °C for 4 h. After cooling, the suspension water (50 mL) was added. The DMF−water phase was extracted with hexane twice. The organic layer was successively washed with saturated $NaHCO_3$ solution (20 mL) and saturated NaCl solution (20 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed in vacuo to give the desired product as a white solid in 90% yield.



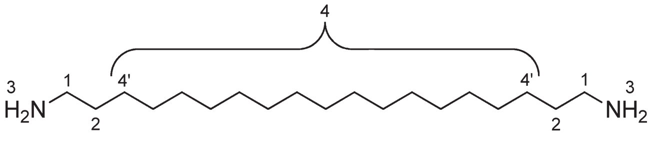
^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 3.24 (t, $^3J_{H-H}$ = 7 Hz, 4H, 1-H), 1.66−1.53 (m, 4H, 2-H), 1.40−1.18 (m, 30H, 3-H).

Tricosane-1,23-diazide. Tricosane-1,23-diazide was prepared analogous to the aforementioned procedure. The desired product was isolated as a white solid in 96% yield.



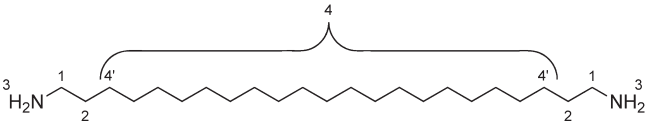
^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 3.25 (t, $^3J_{H-H}$ = 7 Hz, 4H, 1-H), 1.65−1.55 (m, 4H, 2-H), 1.42−1.20 (m, 38H, 3-H).

Nonadecane-1,19-diamine. Nonadecane-1,19-diazide (7.2 mmol, 2.5 g) and Pd/C (10 wt %) (250 mg, 0.23 mmol Pd) were weighed under air into a dry Schlenk tube. In an argon counter stream dry and degassed THF (70 mL) was added. The resulting mixture was cannula-transferred into a 280 mL stainless steel mechanically stirred (1500 rpm) pressure reactor equipped with a glas inlay and a heating/cooling jacket controlled by a thermocouple dipping into the reaction mixture, which was purged several times with argon prior to the reaction. The reactor was closed and pressurized with 20 bar hydrogen and heated to 40 °C. After 3 h the reactor was cooled to room temperature and vented. The reaction mixture was then filtrated repeatedly over a Büchner funnel at 50 °C to remove catalyst residues. The solvent was removed in vacuo to afford an off-white solid, which was recrystallized from ethanol to give the desired product in 83% yield.



^{1}H NMR (dmso-d_6, 130 °C, 400 MHz): 2.59 (t, $^3J_{H-H}$ = 6.5 Hz, 4H, 1-H), 1.41−1.34 (m, 4H, 2-H), 1.33−1.25 (m, 30H, 4-H). ^{13}C NMR (dmso-d_6, 130 °C, 101 MHz): δ 40.82 (C-1), 32.33 (C-2), 28.36−28.07 (C-4), 25.69 (C-4′).

Tricosane-1,23-diamine. Hydrogenation of tricosane-1,23-diazide was carried out analogous to the aforementioned procedure. Tricosane-1,23-diamine was isolated as an off-white solid that was recrystallized from ethanol to give the desired product in 82% yield.



^{1}H NMR (dmso-d_6, 130 °C, 400 MHz): 2.59 (t, $^3J_{H-H}$ = 6.5 Hz, 4H, 1-H), 1.41−1.34 (m, 4H, 2-H), 1.33−1.27 (m, 38H, 4-H). ^{13}C NMR (dmso-d_6, 130 °C, 101 MHz): δ 40.88 (C-1), 32.51 (C-2), 28.38−27.98 (C-4), 25.70 (C-4′).

Polymerization Experiments. *Polyesters.* Polyesters were prepared in a 100 mL two-necked Schlenk tube equipped with an overhead stirrer. Efficient mixing of the highly viscous polymer melt was achieved by a helical agitator. Under a static argon atmosphere the monomers (2.8 mmol of dimethyl 1,19-nonadecanedioate or diethyl-1,23-tricosanedioate, respectively, and 2.8 mmol of α,ω-diol) were filled into the reaction vessel and molten by heating to 100 °C. A 0.4 mL aliquot of a 0.28 M titanium(IV) butoxide solution in toluene was injected, and the temperature was raised to 180 °C over 2 h. In the course of an additional 10 h the temperature was slowly increased to 220 °C. Finally, the polymer melt was stirred for about 2 h at this temperature under reduced pressure (0.01 mbar). Poly[1,6-hexadiyl-1,23-tricosanedioate]: T_m 92 °C, T_c 75 °C, and ΔH_m 145 J g^{-1}. Poly[1,6-hexadiyl-1,19-nonadecanedioate]: T_m 86 °C, T_c 72 °C, and ΔH_m 152 J g^{-1}. Poly[1,12-dodecadiyl-1,23-tricosanedioate]: T_m 100 °C, T_c 76 °C, and ΔH_m 156 J g^{-1}. Poly[1,12-dodecadiyl-1,19-nonadecanedioate]: T_m 93 °C, T_c 76 °C, and ΔH_m 168 J g^{-1}.

Polyamides. Prior to all polymerization reactions the diamine salts of the corresponding dicarboxylic acids were prepared to ensure an exact stoichiometry of these two components. A 10% ethanolic solution of the diamine (1.1 mmol) was slowly added to an equimolar portion of a 10% ethanolic solution of the dicarboxylic acid (1.1 mmol) at elevated temperature, resulting in precipitation of a white solid. The mixture was refluxed for 0.5−1.5 h. After the suspension was cooled to room temperature, the white solid was filtered off, washed with warm ethanol, and dried in vacuo. A 100 mL two-necked Schlenk tube equipped with an overhead stirrer with a helical agitator was charged with the salt, and purged several times with argon. The temperature was raised to 120 °C over 2 h. In the course of another 4 h the temperature was slowly increased to 220 °C, and held for 2 h. Finally, the polymer melt was stirred for about 15 h at this temperature under reduced pressure (0.01 mbar).

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Cif file containing the X-ray diffraction data of **1** (CCDC-817578). This material is available free of charge via the Internet at http://pubs.acs.org.

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