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Authors: Ye Liu and Stefan Mecking

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Synthetic Polyester from Plant Oil Feedstock by Functionalizing Polymerization

Ye Liu, and Stefan Mecking*

Abstract: Catalytic functionalization/polymerization of castor oilderived undecenol yields an aliphatic polyester in a single step under mild conditions. The key to selective formation of linear high melting polyester is highly active carbonylation catalysts that at the same time do not undergo strong isomerization.

Thermoplastic polymers are currently prepared almost exclusively from fossil feedstocks. In view of their limited range, alternative renewable sources are desirable in the long term.^[1-3] Polvesters are one of the most important classes of polvmers. and indeed the more recently developed and commercialized biomass-based polymers are thermoplastic polyesters.^[3-6] The preparation of the corresponding monomers can employ a fermentation step, with carbohydrate, most often glucose, as a feedstock.^[7] By comparison to fermentation, chemical synthetic routes in which the original molecular structure of the plant biomass employed is substantially retained are attractive as they can be efficient in terms of feedstock utilization and reaction. space-time-yields, and provide novel properties. Particularly, fatty acids from plant oils can yield longer methylene sequences as a repeat unit motif.^[8,9] Targeting polymers, a further functionalization in addition to the carboxy group originating from the fatty acid feedstock is required in order to obtain difunctional repeat units.



Scheme 1. Carbonylation polymerization of undecenol derived from castor oil. To enhance the utilization of renewable feedstocks, straightforward synthetic schemes are desirable. We now report on an efficient functionalization and polymerization in a single step via alkoxycarbonylation of undec-10-ene-1-ol (Scheme 1). The latter is readily available from castor oil by thermal cracking and hydrogenation.^[10] However, a functionalizing polymerization to date requires high pressure (200 atm) and temperature (160 °C), using $[Co_2(CO)_8]$ as a catalyst, and unselectively forms a

[*]	Dr. Ye Liu, Prof. Dr. Stefan Mecking
	Chair of Chemical Materials Science, Department of
	Chemistry, University of Konstanz
	Universitätsstraße 10, 78457 Konstanz (Germany)
	E-mail: stefan.mecking@uni-konstanz.
	Dr. Ye Liu, present address:
	State Key Laboratory of Fine Chemicals
	Dalian University of Technology
	Dalian 116024 (China)
	Supporting information for this article is given via a link at the end of
	the document.

branched polymer microstructure.[11]



 $\label{eq:scheme 2. Suggested formation of the active species from a diphosphine-coordinated Pd(II) catalyst precursor, accounting for the adverse effect of excess aldehyde. P^P is e. g. dtbpx (bis(di-tert-butyl)phosphino-o-xylene).$

Alkoxycarbonylation of olefins in principle is a well studied reaction. It is used industrially for the production of methyl propionate from ethylene, CO and methanol.^[12,13] Compared to ethylene, substituted olefins are less reactive, but a number of advanced catalyst systems have been reported recently.[14-16] These can even isomerize an internal double to selectively form the product ester group at a remote position, e.g. methyl oleate can be carbonylated to the terminal linear 1,19-diester.[17-19] Notwithstanding this background, the target reaction poses several challenges. Catalysts that are highly active and/or terminal selective in olefin alkoxycarbonylation are also often very active for isomerization.^[20,21] For example, the industrially extremely active catalyst used for ethvlene methoxycarbonylation with methyl oleate as a substrate affords the aforementioned isomerizing alkoxycarbonylation. With undecenol as a substrate for polymerization, double bond isomerization can be detrimental when it converts this substrate to undecanal. Formation of this saturated aldehyde not only consumes monomer, but also via acetal formation with two further molecules of substrate can disturb the stoichiometric balance vs. the intial AB-monomer composition.



Figure 1. ¹H NMR (left) and ³¹P{¹H} NMR (right) spectra of CD₂Cl₂ solutions of [(dtpbx)Pd(OTf)₂] containing an excess (40 equiv.) of methanol (bottom), undecanol (center), and undecenol (top), respectively (room temperature).

To probe these anticipated issues, the well-established isomerization active carbonylation catalyst based on the bulky electron rich diphosphine dtpbx was studied in NMR tube experiments. Dissolution of the single component precursor

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[(dtpbx)Pd(OTf)₂] in a CD₂Cl₂/methanol mixture resulted in clean complete conversion to the hydride complex [(dtpbx)PdH(solvent)]⁺, in agreement with previous studies^[20] (Scheme 2 and Figure 1, bottom. Note that Pd-H formation is already observed with 1 eq MeOH, and is complete with only 10 equivalents). As expected the resulting hydride solution is very active for olefin isomerization, as probed by addition of 1-decene (cf. Supporting Information, Table S2, entries 13-18). Higher alcohols are known to be less reactive, but also with undecanol instead of methanol the hydride is formed cleanly (Figure 1, center). This suggests that the hydroxyl function of the undecenol monomer is also capable of activating the catalyst precursor to the active hydride species effectively. However, with undecenol as the alcohol component, no hydride species were observed (Figure 1, top). ¹H NMR resonances at 4.46 and 9.77 indicate the formation of aldehyde and acetal products (Figures S1 and S3). The reducing agent in Pd-hydride formation is considered to be the alcohol present, even though the expected (aldehvde) stoichiometric organic products have not been confirmed.^[22] However, addition of excess nonanal to separately prepared Pd-H species results in their consumption (Figure S2), and the same is expected for undecanal formed by isomerization of the monomer. This NMR scale observation is in accordance with low efficiency towards carbonylation with dtbpxbased Pd catalysts in pressure reactor experiments (vide infra). For the case studied here, the adverse effect of aldehyde can be Table 1. Carbonylation polymerization of undec-10-en-1-ol.[a]

accounted for a reversal reaction of the formation for the active species (Scheme 2).



Scheme 3. Diphosphines studied in this work

In view of these partly contradictive requirements, a range of diphosphines (Scheme 3) anticipated to vary in their propensity for isomerization and terminal carbonylation were studied for the targeted carbonylation polymerization of undecenol in pressure reactor experiments (Table 1). Indeed, with dtpbx and related structures (bpx and dtbpp), only small amounts of low molecular weight polyesters are formed and significant aldehyde formation occurs (entries 1-3). By contrast with pytbpx¹⁴ – known to be extremely reactive in olefin methoxycarbonylation – polyester is formed as the major product (entries 4-6). This is surpassed by xantphos, which converts the undecenol completely to polyester that also has a substantially higher molecular weight of M_n 1.7 x

Entry	diphosphi	Temp	CO (bor)	Time	Con. to (%) ^[b]		Polyester			$M_{\rm w}/M_{\rm n}^{\rm [d]}$	$T_{\rm m}$	
	në liganu	(-C)	(bar)	(1)	polyest er	aldehyde and acetal	isomerized olefin	yield (g)	Sel. (%) ⁶³	(kg/mol) ^{es}		(-0)
1	dtbpx	90	30	24	29	24	47					
2	bpx	90	30	24	43	5	53	<0.1	98	1.7	1.2	
3	dtbpp	90	30	24	39	33	28		90			
4	pytbpx	90	30	24	90	0	10	1.6	89	3.3	1.5	64, 70
5	pytbpx	90	30	72	95	0	5	1.7	86	2.7	1.9	65, 68
6	pytbpx	120	30	24	89	<1	11	1.3	86	4.1	1.4	61, 67
7	xantphos	90	30	24	99	0	2	1.7	71	10.3	1.8	55, 60
8	xantphos	120	30	24	>99	0	0	1.9	71	13.6	1.8	55, 63
9	xantphos	120	30	48	>99	0	0	1.9	70	17.4	1.8	54, 60
10	xantphos	50	30	48	33	0	15	<0.1				
11	xantphos	120	20	24	>99	0	1	1.9	71	12.9	1.7	56, 63
12	xantphos	120	10	24	97	0	3	1.6	74	5.8	1.5	56, 63
13	doapp	90	30	24	47	0	53	<0.1	88	1.8	1.2	51
14	adtbpb	90	30	24	88	<1	12	1.5	98	3.3	1.4	73, 75
15	adtbpb	90	10	24	82	3	15	1.0	98	3.1	1.3	68, 71
16	tbcypb	90	30	24	68	10	22	0.9	89	1.22	1.9	50, 55

^aReaction conditions: PdOAc₂/diphosphine/MSA/olefin = 1/2/10/500, molar ratio,1.9 g undec-10-en-1-olin 4.0 mL toluene. ^bDetermined by ¹H NMR. ^cDetermined from integration of ¹³C NMR carbonyl resonances. ^dDetermined by GPC in THF, calibrated with polystyrene standards. ^eDetermined by DSC.

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10⁴ g mol⁻¹ (entry 9). Note that this value is on the same order as molecular weights of commercial polyester materials. A molecular weight distribution of M_w/M_n close to 2 indicates a well behaved nature of the catalytic polycondensation reaction. Differences in the melting points (Table 1) of the polyesters obtained with different diphosphines can be related to their linearities. Branched units that disturb crystallization, resulting from carbonylation of a secondary alkyl, are mainly present in the form of methyl branches (Figures 2, S6-S9, S23 and S25). Notably, with the mixed-substituted benzyl backbone adtbpb, formation of virtually entirely linear polyester was possible. Hereby, a peak melting point of T_m 75 °C could be achieved (Table 1, entries 14 and 15, Figure S27). This matches with a linear polyester sample prepared by traditional polycondensation of 12-hydroxydodecanoic acid for comparison.^[23]

Note that a high isomerizing ability (problematic in this carbonylation polymerization) and a high linear selectivity (desirable) are not contradictive (also cf. entry 2 with bpx), but in alkoxcarbonylation of olefins in general often go hand in hand, as selectivity depends on the preference for CO insertion into the terminal alkyl vs. branched alkyls.

End group analysis of the polyesters by TOSCY and DOSY NMR spectroscopy and MALDI-TOF spectrometry (Figures S10-S14) reveals terminal –OH and internal olefin end groups. Molecular weights from NMR spectroscopy agree reasonably well with molecular weights determined by GPC, considering that GPC vs. polystyrene standards usually overestimates molecular weights for hydrocarbon backbone polymers. A considerable deviation is found for the higher molecular weight polyesters formed with xantphos. This is due to cycle formation, as evident from MALDI-TOF (Figure S15). It is well established that in polycondensations a considerable portion of cycles are formed when high conversions are achieved, and the concentration of reacting groups is very low which favors intramolecular cyclization.^[24,25]



Figure 2. ¹³C NMR carbonyl resonances of polyesters obtained with different diphosphine ligands: adtbpb (bottom; Table 1, entry 14), pytbpx (center; Table 1, entry 6); and xantphos (top; Table 1, entry 9).

In view of these findings, the isomerization behavior of selected catalysts was studied further by NMR spectroscopy, under conditions similar to pressure reactor polymerizations (but in the absence of CO). In all cases, isomerization of the terminal double bond of the undecenol substrate occurred even at room temperature or slightly above, and at 90 °C no terminal olefin remained. However, only with dtbpx and also adtbpb (though less rapid) full isomerization across the entire C_{11} chain to form the aldehyde occurred, while this was not the case for xantphos and pytbpx (Figure S4). The identified microstructures of polyesters formed with different diphosphine ligands are confirmed by selectivities observed in alkoxycarbonylation of model olefins (1- and 2-octene) with undecanol (Figure S16).

In summary, carbonylation polymerization of undecenol can yield polyesters at moderate conditions, namely 10 to 20 atm of CO pressure with virtually full conversion of the substrate to the desired polyester. In general terms, any polycondensation requires sufficient reaction rates even at low concentrations of the reacting groups, as present in the final stages of the reaction. to achieve reasonably high molecular weights. It is notable that the catalytic carbonylations studied here can fulfill this criterion. The key to achieving these high conversions is catalysts very active for carbonylation, which at the same time do not promote extensive isomerization. The latter results in loss of monomer and catalyst deactivation by the aldehyde formed. Despite these constraints, even high linearities and consequently higher melting points can be achieved with appropriately chosen catalysts. The case of adtbpb shows that in achieving this a certain propensity for isomerization can be tolerated, providing that carbonylation is competitive with isomerization. This can also serve as a guideline for further developing this chemistry.

Experimental Section

Carbonylation polymerization was carried out in a 20 mL stainless steel reactor equipped with a glass inlet and a magnetic stirring bar, heated in a metal block. The reactor was purged repeatedly with nitrogen. Undec-10-en-1-ol, Pd(OAc)₂, additional diphosphine ligand, methanesulfonic acid (MSA) and toluene were weighed in a Schlenk tube equipped with a magnetic stirr bar in a glovebox. The mixture was stirred vigorously and cannula-transferred into the reactor in a nitrogen stream. A static pressure of 20-30 bar CO was applied, and the reactor was heated to the desired temperatures under stirring. After the designated reaction time, the reactor was cooled to room temperature and the CO pressure was released slowly. An aliquot was taken out and CDCl3 was added for NMR spectroscopy analysis to determine conversion and the product distribution. The reactor and glass inlet were washed with dichloromethane, and the combined phases were removed in vacuum. To completely remove any unreacted monomer which could disturb further analysis, the remaining crude polymer was repeatedly redissolved in dichloromethane, precipitated with methanol, isolated by filtration, and washed several times with methanol. The collected polymer was dried in vacuum at 50 °C prior to determination of the yield by weighing and NMR, GPC and DSC analysis.

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