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Copolymerization of ethylene with terminally unsaturated fatty acid derivatives

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Introduction

Incorporation of polar comonomers expands the scope of polyolefins referring to adhesion, dyeability or compatibility with additives or more polar polymers in blends. Commercially available copolymers from ethylene and mainly vinyl acetate, acrylic and methacrylic acid and their derivatives are produced by radical polymerization at elevated temperatures and high pressure /1/. Low pressure insertion-type copolymerization with heterogeneous Ziegler or homogeneous metallocene/aluminoxane catalysts can only be achieved by using a few monomers which minimize interaction with the Lewis acidic catalyst sites. Several homo and copolymers are available by using borane monomers and post polymerization transformation to polymer alcohols, amines, halides, aldehydes and nitriles /2/. The use of sterically hindered esters, alcohols, phenols and amines enables polymerization as well whereas comonomers with active hydrogens are made accessible to insertion polymerization by precomplexation with organoaluminium compounds /3/. Latest developments of late transition metal complexes with sterically bulky diimine ligands (see Fig. 1) by Brookhart and coworkers show much improved tolerance against polar functionality due to their typically less Lewis acidity /4/.

Copolymerization of ethylene with ω -unsaturated fatty acid methyl esters, available by metathesis of natural fatty acid esters from rapeseed oil and high oleic sunflower oil with ethylene /5/, was studied using one

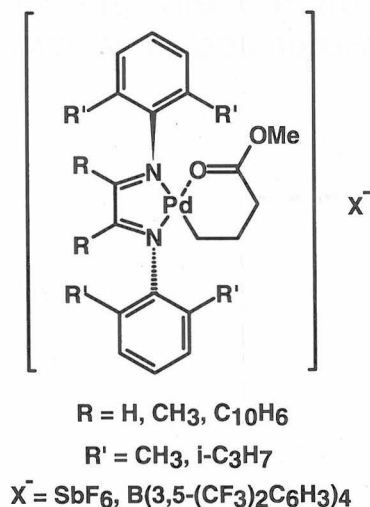


Fig. 1: Monocationic Palladium "Brookhart"-catalysts

of these catalysts. These substrates are useful comonomers for this purpose, because methylene spacers reduce the interaction between the polar group and the active centre of the catalyst. α,ω -unsaturated diesters achieved by transesterification with ethylene or 1,4-butylene glycole (see Fig. 2) were copolymerized with ethylene receiving polar, partially crosslinked polyethylenes for polyolefin rubber applications.

Methods

All synthetic procedures were performed under argon using standard Schlenk-techniques. Catalyst was prepared according to literature /4/. Incorporation of polar comonomers was by determined by ¹H-NMR (Bruker AMX 300 (300 MHz, 20 °C, in CDCl₃ or d⁸-THF)). Molecular weights were measured on a GPC/SEC equipment (10,000, 1,000 and 100 Å columns, refraction index and light scattering detector) using THF as the eluent (flow rate: 1 ml/min) versus polystyrene calibration stan-

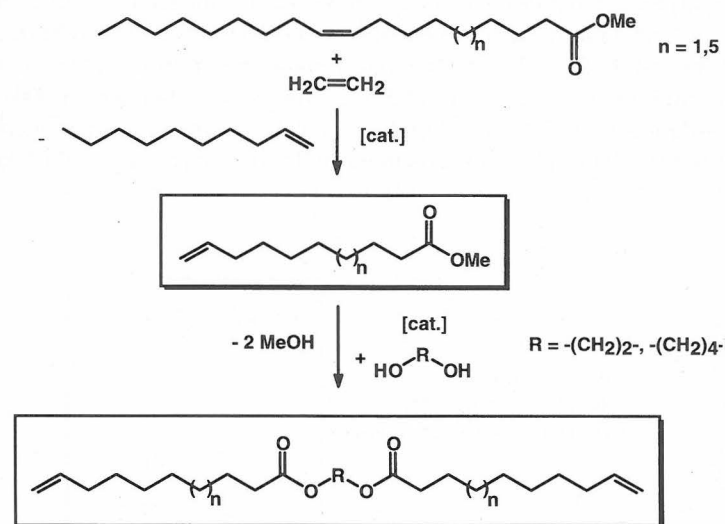


Fig. 2: Synthesis of ω -unsaturated fatty acid methyl esters and α,ω -unsaturated diesters from natural fatty acid methyl esters

dards. Differential scanning calorimetry was carried out on a Mettler TA 3000 instrument at a heating rate of 10 °C/min using open crucibles.

Results

Terminally unsaturated fatty acid methyl esters and α,ω -unsaturated diesters efficiently undergo copolymerization with ethylene under mild conditions (2.5 bar, room temperature) using the cationic Palladium catalyst $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdC}_3\text{H}_6\text{COOMe}\}\text{SbF}_6$ (see Fig.1). Copolymerization of ethylene with terminally unsaturated methyl esters was carried out at a mole ratio of 350 (ester/Pd). To enable comparison, copolymerization using polar α,ω -dienes was run at a mole ratio of 175 (diene/Pd). Further experiments studying the effect of comonomer concentration indicated optimum conditions at these ratios with regard to comonomer incorporation, conversion and molecular weight.

Copolymers from ethylene and 9-decenoic, 10-undecenoic and 13-tetradecenoic acid methyl esters were obtained with molecular weights from 32,000 to 76,000 g/mol, conversions of comonomer from 32-53 % and comonomer incorporations from 1.7 to 2.2 mol% (12.2-14.3 wt-%) (Tab.1). In accordance with literature, copolymers were random, highly branched (80-120 CH₃/1000 CH₂) with functionality located at the end of the branches /6/ as determined by ¹H-NMR (see Fig. 3).

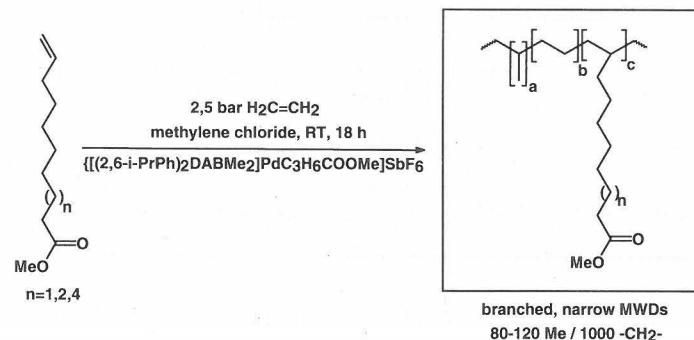


Fig. 3: Copolymerization of ethylene and ω -unsaturated fatty acid methyl esters

Molecular weight distributions (MWDs) were generally narrow ($M_w/M_n = 1.2-1.5$). Catalyst activities decayed to 55-65% of the corresponding homopolymerization activity (run 5). In order to estimate the influence of ester functionality on catalyst activity, homopolymerization of ethylene was run using capric acid methyl ester under otherwise identical conditions. Whereas the molecular weight was not significantly reduced, catalyst activity decreased comparably to copolymerization. Furthermore, copolymerization of ethylene and acrylic acid methyl ester was performed (run 4) with considerably lower catalyst activity and drastically lower comonomer conversion ($TON_{ester} = 7$; 2 % conversion) and incorporation in comparison with oleochemical ω -alkenoates.

Copolymerization of ethylene and α,ω -diesters lead to partially crosslinked, branched, high molecular weight polymers (see Fig. 4). Incorporations of 0.7-1.75 mol-% (9-20 wt-%) and comonomer conversions of

39-67 % were achieved (Tab. 2). Whereas catalyst activities were comparable with copolymerization using ω -alkenoates, molecular weights were determined considerably higher, four to sixteenfold higher than ethylene homopolymerization. The MWDs are remarkably broader ($M_w/M_n=4-13$) emphasizing the crosslinked structure. Incomplete crosslinking was indicated by remaining olefin signals detected by ¹H-NMR.

Table 1: Copolymerization of ethylene and ω -unsaturated fatty acid methyl esters (Cat.: [[2,6-i-PrPh)₂DABMe₂]PdC₃H₆COOMe]SbF₆)

run	comonomer	activity [kg/mol]	incorporation [mol-% (wt-%)]	TON C=C	TON ester	M_w^a [g/mol]	M_w/M_n
1	9-DME	226.3	2.19 (12.1)	8,046	168	62,790	1.15
2	10-UME	225.0	2.37 (14.3)	7,799	186	75,570	1.20
3	13-TME	189.0	1.68 (13.3)	6,531	111	32,620	1.42
4	AME	135.5	0.13 (0.5)	5,202	7	46,030	1.68
5	-	345.8	- (-)	13,980	-	106,200	1.15
6	- ^b	244.8	- (-)	9,858	-	91,420	1.18

20 °C, 2.5 bar ethylene, methylene chloride, 40 μ mol Pd-catalyst,

14 mmol ω -unsaturated acid methyl ester

9-DME: 9-decenoic acid methyl ester; 10-UME: 10-undecenoic acid methyl ester

13-TME: 13-tetradecenoic acid methyl ester; AME: acrylic acid methyl ester

a. based on polystyrene-calibration standards

b. 14 mmol capric acid methyl ester

Properties

Ester copolymers were tacky, highly viscous oils, which are easily soluble in polar organic solvents like THF, ether, MTBE and halogenated hydrocarbons. Diester copolymers had a tacky nonflowing, rubberlike physical appearance and are worse soluble in THF. Thermal data are summarized in Tab. 3. indicating viscoelastic properties of all copolymers. Substances exhibited significantly low glass transition temperatures from -65 to -35 °C which are typical of comblike or branched polyolefins. Glass transition temperatures were partially superimposed by broad low temperature melting endotherms (-39 up to 0 °C) due to partial crystallites. Low

Table 2: Copolymerization of ethylene and α,ω -unsaturated fatty acid diesters (Cat.: $\{[(2,6\text{-}i\text{-PrPh})_2\text{DABMe}_2]\text{PdC}_3\text{H}_6\text{COOMe}\}\text{SbF}_6$)

run	α,ω -diene	activity [kg/mol]	incorporation [mol-% (wt-%)]	TON C=C	TON diester	M_w^a [g/mol]	M_w/M_n
7	EDD	215.9	1.29 (12.9)	7,606	86	1,516,000	5.6
8	EDU	234.3	0.88 (11.0)	8,213	74	374,900	4.2
9	BDD	205.6	1.75 (19.8)	6,739	118	592,300	5.3
10	BDU	251.1	0.73 (9.4)	9,204	68	1,146,000	13.3

20 °C, 2.5 bar ethylene, methylene chloride, 40 μmol Pd-catalyst, 7 mmol α,ω -unsaturated acid methyl ester
 EDD:ethylene di-9,9'-decanoate EDU:ethylene di-10,10'-undecenoate
 BDD:butylene di-9,9'-decanoate BDU:butylene di-10,10'-undecenoate

a. based on polystyrene-calibration standards

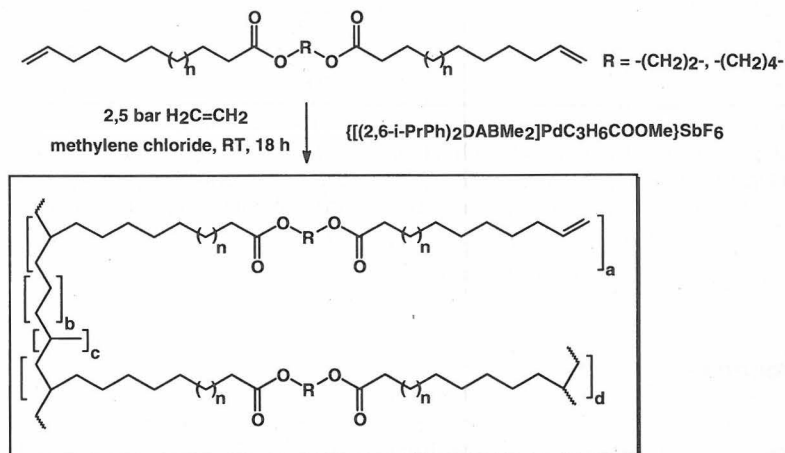


Fig. 4: Copolymerization of ethylene with α,ω -unsaturated diesters

glass transition temperatures and melting ranges show potential for low temperature applications. No further melting was observed until decom-

position started at temperatures from 155 to 235 °C. Therefore, copolymers are suitable for adhesives, lubricants or polymer blends.

Table 3: Thermal data of several copolymers

Comonomer	T_g [°C]	T_m [°C]	T_d [°C]
9-DME	-	-36	155
10-UME	-	-39	187
13-TME	-65	-35	180
EDD	-54	-30/0	180
EDU	-45	-25	180
BDD	-45	-23	235
BDU	-	-19	175

T_g : glass transition temperature; T_m : melting temperature; T_d : decomposition temperature

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