

Metallocene Catalysts for Olefin Oligomerization

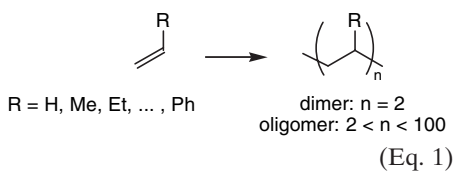
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Summary: Metallocene complexes with a cocatalyst such as methylalumoxane, MAO can be used as catalysts in the dimerization or oligomerization of olefins (alkenes) including the (co-/hydro-)oligomerization of ethene, of the α -olefins propene, 1-butene, 1-pentene, 1-hexene, and higher α -olefins, branched α -olefins, cyclic olefins and α,ω -dienes. Possible applications of α -olefin oligomers are summarized. Oligo-olefins can be analyzed by gel permeation chromatography (GPC) or ^1H NMR spectroscopy for molecular weight determinations and by ^1H and ^{13}C NMR spectroscopy or MALDI-TOF mass spectrometry for their end group structure.

Keywords: 1-hexene; MALDI MS; metallocene catalysts; oligomers; propene

Introduction

The interest in the catalytic oligomerization of olefins comes from the use of olefin oligomers as building blocks and intermediates for specialty chemicals.^[1,2] α -Olefinic ethene oligomers of chain lengths C_4 – C_{18} are manufactured in the SHELL-higher-olefin-process (SHOP).^[1,3] The C–C coupling of olefins according to eq. 1 is categorized as dimerization when $n=2$, oligomerization when $2 < n < 100$ and polymerization when $n > 100$.^[1]



Metallocene catalysts, in particular zirconocene complexes with an appropriate cocatalyst,^[4] can be used effectively for the direct oligomerization of α -olefins^[5–18] and other monomers, although in the beginning of polymerization by metallocene catalysis, oily, oligomeric or low molar-mass products from propene polymerizations with zirco-

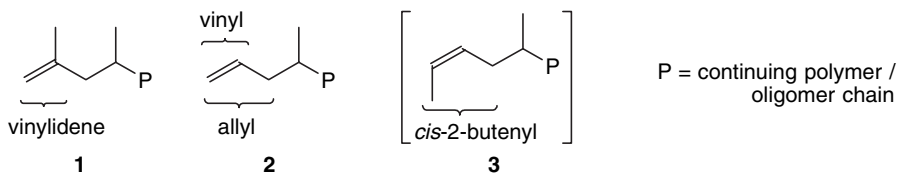
nocene catalysts was generally regarded as unfortunate^[19,20] and to some extent still is. By now it is more and more recognized that the single-site feature of metallocene catalysts may also be useful in organic synthesis of olefin dimers and oligomers. The catalytic olefin coupling process is diverted from a rapid polymerization to dimerization and oligomerization by the drastic increase in the rate of termination versus the rate of propagation.^[6]

With metallocenes the chain-termination reactions can give oligomers with unsaturated, double-bond end groups, predominantly of the vinylidene type (**1**). In special cases also a vinyl/allyl double-bond (**2**) or a 2-butenyl group (**3**) can be formed.^[21] One way to enforce oligomers is to use hydrogenation, that is, hydrogenolysis of the M–R bond as an additional termination reaction. But this has the disadvantage of yielding unfunctionalized, saturated hydro-oligomers.

Metallocene Catalysts for Olefin Oligomerization

Summarily we note the use of metallocene catalysts in the oligomerization of ethene,^[22–24] in the ethene/ α -olefin co-oligomerization,^[16,25,26] in the dimerization and (hydro-)oligomerization of 1-butene,^[8,14,27,28] 1-pentene,^[14,15,28,29] and 1-hexene^[5,6,14,16,22,30–32] (for details and higher α -olefins, branched

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α -olefins, cyclic olefins and α,ω -dienes see ref. [21]). Individual metallocene catalysts and some details for propene oligomerization are provided in Table 1.

Oligomer Applications

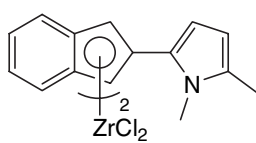
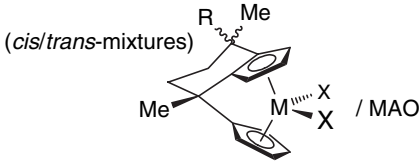
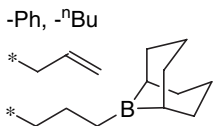
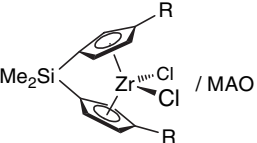
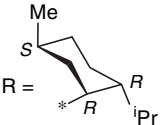
Possible applications for olefin oligomers are feedstocks for surfactants, clean diesel fuel alkanes,^[53] octane boosters and new monomers.^[54] Functionalization reactions with

(usually vinylidene) double-bond end groups in oligomers (Scheme 1) lead to organic specialities with potential applications as adhesives,^[55] blend compatibilizers,^[10,11,56] fragrances, synthetic lubricants,^[18,25,57] additives for fuels^[57] or in the paper and leather industry.^[5,58] Derivatives of α -olefin oligomers (obtained through a chain end functionalization/double bond conversion) can be used as (macro-)monomeric building blocks

Table 1.
Metallocene complexes for the oligomerization of propene.^{a)}

| Metallocene | Remarks | Ref. |
|--|---|----------------------|
| $(C_5H_5)_2ZrCl_2$ / MAO | most employed system | 6,10–12, 17,33–35 |
| $(C_5H_5)_2ZrMe_2$ / MAO | | 16,22 |
| $(C_5H_5)_2ZrCl_2$ / EAO or $AlEt_3$ | cyclic trimeric products | 36 |
| $(C_5H_5)(C_5H_5-nMe_n)_2ZrCl_2$ / MAO; $n=1-5$ | comparative study on methyl substitution; | 16,20,30, |
| $(C_5H_5-nMe_n)_2ZrCl_2$ / MAO; $n=1-5$ | vinyl/allyl end groups from $(C_5Me_5)_2ZrCl_2$ | 32,34,37 |
| $(C_5H_4Me)_2ZrMe(\eta^1-CB_nH_{12})$ | no cocatalyst necessary | 38 |
| $[(C_5Me_5)_2MMe(THT)]^+ [BPh_4]^-$ ($M=Zr, Hf$, THT = tetrahydrothiophene) | no cocatalyst necessary | 39 |
| R = H, cyclo-Pr, tBu, SiMe ₃ , Ph | | 30,32,40 |
| $(C_5H_5)(C_5H_5-n^tBu_n)_2ZrCl_2$ / MAO; $n=1-3$ | comparative study on <i>t</i> -butyl substitution | 6,30,32 |
| $(C_5H_5-n^tBu_n)_2ZrCl_2$ / MAO; $n=1,2$ | <i>rac</i> -like metallocene in the solid state | 41 |
| / MAO R = H, Me, Pr, Ph, cyclohexyl | | |
| $(Ind)_2ZrCl_2$ / MAO | | 16 |
| $(2-PhInd)_2ZrMe_2$ / Al^iBu_3 | | 42 |

Continues

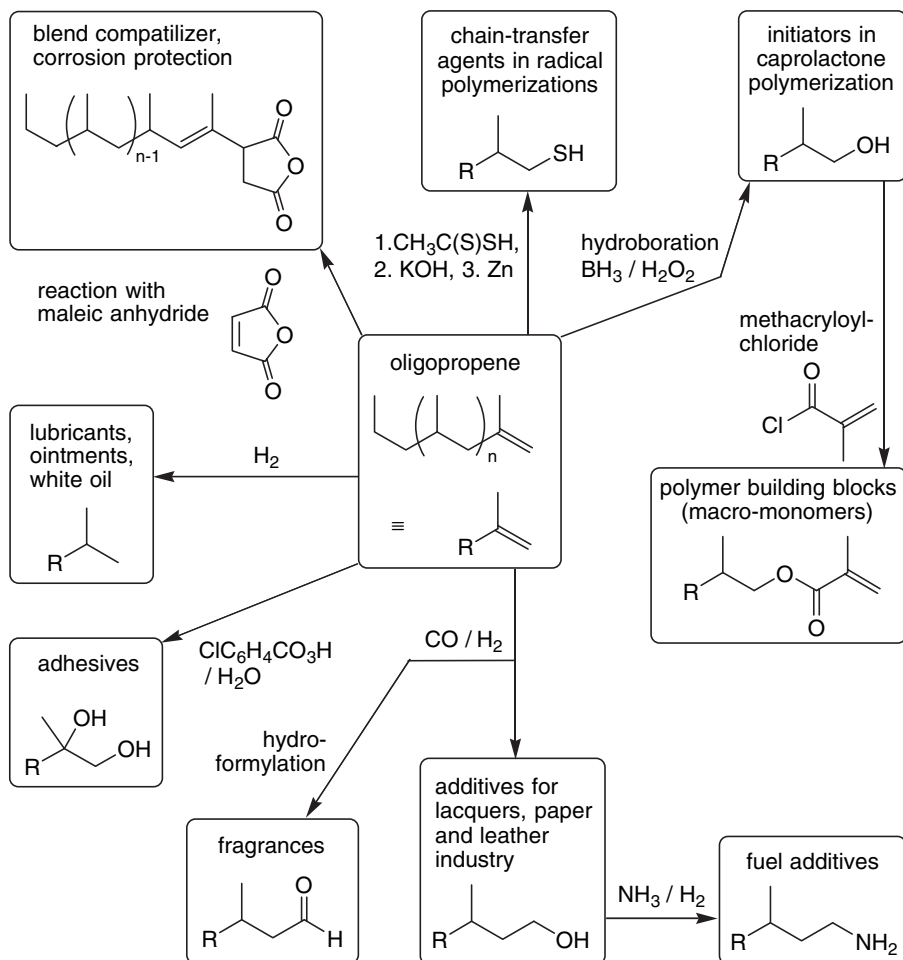
| Metalloocene | Remarks | Ref. | |
|--|---|------------------------------------|---|
|  / MAO | rac-like metallocene in the solid state | 43 | |
|  / MAO | R = Me $\text{MX}_2 = \text{ZrMe}_2, \text{HfMe}_2$ -Ph, - ⁿ Bu  } $\text{MX}_2 = \text{ZrCl}_2$ | 13,44 | |
|  / MAO |  R = | chiral, meso-like ansa-zirconocene | 7 |
| <i>rac</i> -Me ₂ Si(Ind') ₂ ZrCl ₂ / MAO | hydro-oligomerization | 45 | |
| <i>rac</i> -Me ₂ Si(2-Me-benz[e]indenyl) ₂ ZrCl ₂ or <i>rac</i> -Me ₂ Si(benz[e]indenyl) ₂ ZrCl ₂ / MAO | hydro-oligomerization | 46 | |
| (C ₂ H ₄)(2-Ind') ₂ ZrCl ₂ / MAO | various Me substitutions in 1- and 3-position and Ph substitution in 4-position of Ind' | 47 | |
| <i>rac</i> -C ₂ H ₄ (Ind') ₂ ZrCl ₂ / MAO | [C ₃ H ₆] → 0 mol.l ⁻¹ , hydro-oligomerization | 48 | |
| <i>rac</i> -C ₂ H ₄ (Ind') ₂ ZrMe ₂ / MAO | propene from vinyl chloride insertion and β-Cl elimination | 45 49 | |
| <i>rac</i> -C ₂ H ₄ (Ind'H ₄) ₂ ZrCl ₂ / MAO | 99% dimer | 28 | |
| (<i>S</i>)-C ₂ H ₄ (Ind'H ₄) ₂ Zr(O-acetyl-(<i>R</i>)-mandelate) ₂ | / MAO, optically active oligomers for >C ₉ | 8,50 | |
| (<i>R</i>)-C ₂ H ₄ (Ind'H ₄) ₂ ZrMe ₂ / MAO | optically active hydro-oligomers for >C ₉ | 51 | |
| (CH ₂) _n (C ₅ H ₄) ₂ ZrCl ₂ / MAO | ansa-zirconocene, n = 9,12 | 52 | |

^{a)} For further details see ref. [21]. MAO = methylalumoxane. – EAO = ethylalumoxane. – Ind = indenyl. – Ind' = substituted indenyl, 1-indenyl, unless stated otherwise. – Ind'H₄ = tetrahydro-1-indenyl. Hydro-oligomerization means propene polymerization in the presence of H₂ as a chain transfer agent, mostly with the aim of kinetic or mechanistic studies (regioselectivity of last insertion etc.).

for novel graft copolymers containing oligo-olefin side chains: Succinic anhydride-terminated oligopropenes are obtained by enyne-type addition of maleic anhydride. The anhydride-terminated oligopropene reacts with amine-terminated polyamide-6,6 to yield polypropene-*b*-poly-amide-6,6-*b*-polypropene triblock copolymers which are efficient dispersing agents.^[10,11,55] Thiol-terminated oligopropenes are chain transfer reagents in radical methylmethacrylate polymerization. Acrylic monomers and styrene are grown onto the thiol end group via chain transfer reaction, thereby producing a family of block copolymers.^[10,12] Hydroxy-termi-

nated oligopropenes are useful initiators in caprolactone polymerization to form poly(propene-*b*-caprolactone) block copolymers.^[10] Homo- and copolymerization of methacrylate-terminated oligopropene (macromonomer) yield novel classes of graft copolymers with pendant oligopropene chains (Scheme 1).^[10,12]

In addition, olefin oligomerization is used to study mechanistic aspects and to obtain better insight into the reaction mechanism of metallocene polymerization catalysis because of the homogeneity of the reaction mixture (no heterogenation through polymer precipitation) and because



Scheme 1.

Potential functionalizations and applications for specialty chemicals on the basis of oligopropene (olefin oligomers in general; adapted from [5,10]). For further details see references in text.

in some aspects the oligomeric products are easier to investigate than high-molar-mass polymers.^[22,23,30,33,34,37,39,59]

Oligomer Analyses by MALDI-TOF MS

Molecular weight determinations of olefin oligomers are typically based on gel permeation or gas chromatography (GPC, GC), ^1H NMR spectroscopy, viscosity and/or cryoscopy measurements. Assignment of the start and end group structure, which is *inter alia* important for the chain transfer mechanism, is typically based on ^1H , occasionally also on ^{13}C NMR spectroscopy.^[21] In addition, *MALDI-TOF MS*

(matrix assisted laser desorption ionization-time of flight mass spectrometry) can be used to elucidate the chain termination reactions. This method is successful for the characterization of large biopolymers and synthetic polymers.^[60] The ionization technique allows for the investigation of very large and/or thermolabile molecules without fragmentation of the molecular ions. Polyolefins are in principle not susceptible to the MALDI technique because functional groups in the polymer are necessary for the adduct formation with silver (sodium or potassium) ions used for the ionization. In unpolare olefin oligomers

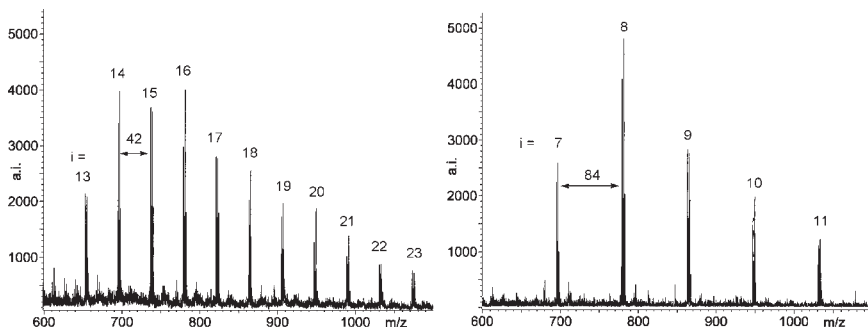


Figure 1.

MALDI-TOF mass spectra for samples of oligopropene (left, obtained with $(C_5H_5)(C_5HMe_4)ZrCl_2/MAO$) and oligo-1-hexene (right, with $(C_5H_5)(C_5H_4^tBu)ZrCl_2/MAO$). Peaks correspond to the silver adduct of M_i (i = degree of oligomerization, number of monomer units; a.i. = arbitrary intensity; silver isotopes ^{107}Ag , abundance 100% and ^{109}Ag , 92.9% lead to the “doublet” isotope distribution).

MALDI-TOF MS promises a potential for analysis because of the double-bond end-group functionality.

Figure 1 shows a typical MALDI-TOF mass spectrum for an oligopropene and an oligo-1-hexene material. The peak separation corresponds to the monomer mass. From the mass/charge minus a whole-numbered multiple of the monomer mass, the residual mass is obtained which corresponds to the start group. Normally the intensity of mass peaks in mixtures is proportional to the molar amount of each species and therefore the mass spectra should yield M_n and M_w/M_n (Q). Indeed the mass spectra in Figure 1 represent a

mass distribution curve. However, it is apparent that the method and the apparatus conditions impose severe limitations with respect to interpreting the olefin oligomer spectra in this direction. The vacuum which is applied before ionization already removes the very low molar mass content from the sample, which is rather critical here. At the same time, the high molar mass end of the sample is also not well reproduced because of the single double-bond functionality together with the detection of the molecular ion as a metal adduct. Thus, olefin oligomers investigated with MALDI-TOF MS give a too small dispersion Q which does not reflect

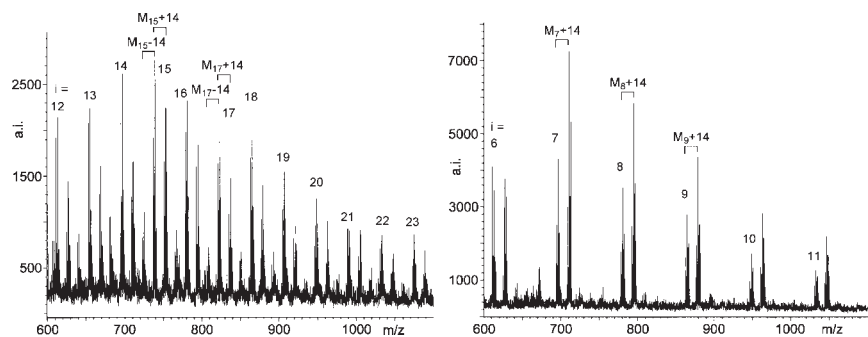


Figure 2.

MALDI-TOF mass spectra for samples of an oligopropene with β -methyl elimination (left, note the M_i+14 and M_i-14 peaks) and an oligo-1-hexene with chain transfer to aluminum (right, note the M_i+14 peak); see also Scheme 2. Both oligomers were obtained with $(C_5HMe_4)_2ZrCl_2/MAO$. Peaks correspond to the silver adduct of M_i (i = degree of oligomerization, number of monomer units; a.i. = arbitrary intensity; silver isotopes ^{107}Ag , abundance 100% and ^{109}Ag , 92.9% lead to the “doublet” isotope distribution).

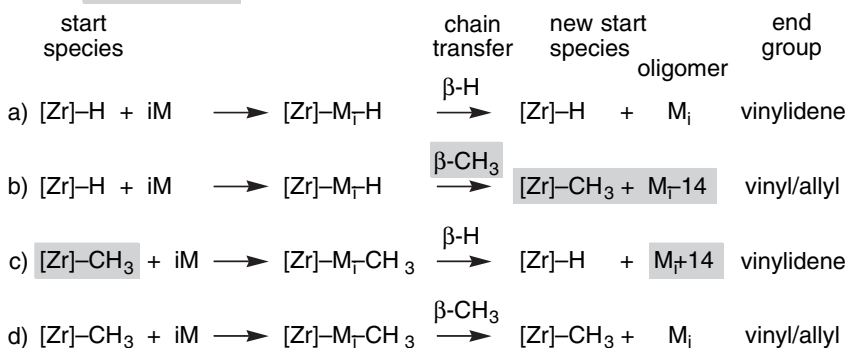
the real molar mass distribution. Still, MALDI-TOF is able to provide valuable information concerning the start and end group of the oligomers and the mechanism of chain transfer as is illustrated in Figure 2 together with Scheme 2.^[30]

Evidence for the β -methyl elimination is obtained in the MALDI-TOF mass spectra by a M_i-14 and M_i+14 peak around M_i in Fig. 2 (left) (M_i = multiples of 42 for propene). The M_i-14 peak originates from an oligomer with a $[Zr]-H$ start group and chain termination by $\beta-CH_3$ elimination (Scheme 2b). Since the latter gives rise to $[Zr]-CH_3$ start groups, a M_i+14 peak is seen

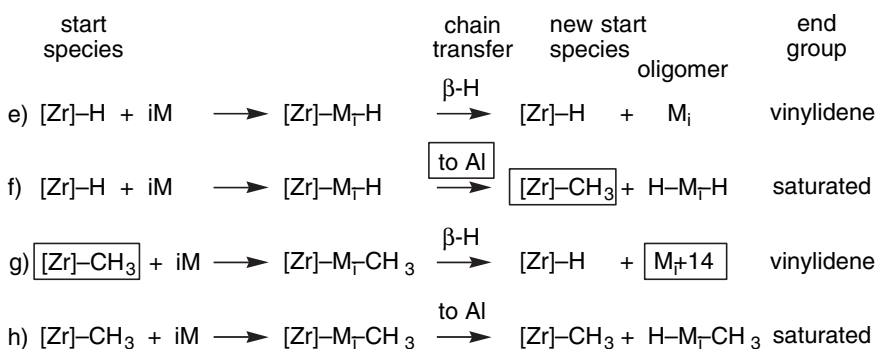
for oligomers which are then terminated by $\beta-H$ elimination (Scheme 2c). The oligomers which start with $[Zr]-CH_3$ and end with $\beta-CH_3$ elimination feature the M_i peak (just like those with a $[Zr]-H$ start group and $\beta-H$ elimination) (Scheme 2a and d).

MALDI-TOF MS can also support the formulation of a chain-transfer to aluminum. Fig. 2 (right) displays a sample spectrum of an oligo-1-hexene which features M_i+14 peaks in addition to M_i peaks. Chain-transfer to aluminum will give rise to saturated end groups which do not show as peaks in the MALDI-TOF MS due to lack of the double-bond functionality

M_i and $M_i \pm 14$ peaks:



M_i and M_i+14 peaks only:



M = monomer; M_i = molar mass of oligomer M_i

Scheme 2.

Correlation between start and end group for the different chain transfer reactions. Species and start/end groups for the $M_i \pm 14$ peaks and the M_i+14 peak are highlighted. Only oligomers with vinylidene or vinyl/allyl end groups can be seen in MALDI-TOF MS. Saturated oligomers do not give an MS peak with this method.

(Scheme 2f and h). The M_i and M_i+14 peaks correspond to oligomers from $[\text{Zr}]\text{-H}$ and $[\text{Zr}]\text{-CH}_3$ start groups, respectively, which are terminated by β -hydrogen elimination (Scheme 2e and g). The relative intensities of the M_i and M_i+14 peaks are a direct measure of the probability or percentage of the chain-termination pathway.

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