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Ethylene/1,3-Cyclohexadiene Copolymerization by Means of Methylaluminoxane Activated Half-Sandwich Complexes

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Summary: Ethylene copolymerization with 1,3-cyclohexadiene (CHD) was investigated by using methylaluminoxane (MAO) activated single-site catalysts including bridged and non-bridged titanium half-sandwich and bimetallic cobalt(I) complexes. MAO activated $CpTiCl_2[N{=}P(^tBu)_3]$ (Cp = cyclopentadienyl, ^{t}Bu = *tert*-butyl) gave high molecular weight CHD copolymers without encountering catalyst activity losses. According to the NMR microstructure investigation the resulting copolymers are highly regioregular.

Keywords: 1,3-cyclohexadiene polymers; cycloolefin copolymers; dienes; ethylene copolymerization; half-sandwich complexes; single-site catalysts

Introduction

Since the early days of Natta and Ziegler progress in catalyst and process technology had significant impact in the synthesis of polyolefin materials. In the last decade the invention of single-site catalysts facilitated the preparation of polymers via catalyst design and fine-tuning of the polymer properties. As a function of single-site catalysts' ligand frameworks the design of novel polymer architectures based upon olefin, diene, styrene and cycloolefin feed stocks provides a rich portfolio of advanced materials with tailored property profiles. Cycloaliphatic homopolymers and cycloolefin copolymers (COC) have attracted considerable interest during the last decade. Novel and conventional transition metal systems are used in ring opening metathesis polymerization (ROMP) to prepare cycloolefin homo- and copolymers. Hydrogenated ROMP polymers with rigid cycloaliphatic units in the polymer backbone are suitable as thermoplastic glass substitute used in optical and electrooptical applications. Ni- and Pd-catalyzed homo- and copolymerization of norbornene and norbornenes derivates give rise to high-performance optical polymers. Cyclopolymerization of 1,4- and 1,5-dienes accounts for an alternative pathway to COCs. In contrast to the ROMP/hydrogenation approach, the access to COCs via ethylene/cycloolefin copolymerization by using single site catalysts is a one-step synthesis. COC architectures have been realized on the basis of norbornene, cyclopentene and other mono- and multicyclic feedstocks.[1]

In comparison to COC containing five-membered rings, much less is known about polyolefins containing six-membered rings in the backbone. In a recent advance for thefirst time cyclohexene was copolymerized with ethylene in the presence of MAO

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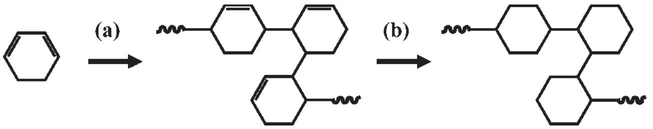

Figure 1.
(a) CHD homopolymerization resulting in polycyclohexadiene with 1,2- and 1,4- enchained rings and (b) subsequent hydrogenation.

activated Cp′TiCl$_2$(OAr) (Cp′ = indenyl, ^{t}BuC$_5$H$_4$, 1,2,4-Me$_3$C$_5$H$_2$; OAr = -O-2,6-^{i}Pr$_2$C$_6$H$_3$).[2] The homopolymerization of 1,3-cyclohexadiene (CHD) and subsequent hydrogenation of the resulting polymer offers an alternative access to cycloaliphatic polymers comprising cyclohexane units in the main-chain (Figure 1).[3] Anionic CHD homo- and copolymerization with styrene and acyclic dienes results in regioirregular homo- and cycloolefin copolymers containing both 1,2- and 1,4-enchainment of cyclohexane rings. Although the addition of amines to the anionic CHD homopolymerization improved the regioselectivity, the resulting molecular weight in these polymers do not exceed $M_n = 77{,}000$ g/mol.[4]

CHD homopolymerization by means of late and early transition metal catalysts affords high molecular weight polycyclohexadienes with improved control of regioselectivity. However, in some cases highly regio- and stereospecific catalysts produce crystalline, high molecular polycyclohexadienes insoluble in common organic solvents, as reported for nickel systems.[5,6] Since the melting temperatures were higher than temperature of thermal degradation, those regio- and stereoregular copolymers were not melt processable. By using the constrained geometry catalyst [(Me$_4$Cp)SiMe$_2$N(^{t}Bu)]TiCl$_2$ (CBT) in combination with methylaluminoxane (MAO) it is possible to generate soluble high molecular weight polycyclohexadienes and CHD/ethylene copolymers.[6] In this paper we focus the use of novel single-site catalysts in CHD/ethylene copolymerization. The influence of the catalyst on activity, CHD incorporation, molecular weight and regioselectivity are discussed.

1,3-Cyclohexadiene/Ethylene Copolymerization

In general, 1,2- as well as 1,4-insertion of CHD can take place in copolymerization with ethylene (Figure 2). Recently we demonstrated that CBT activated with MAO affords high molecular weight CHD/ethylene copolymers with up to 12 mol-% of CHD incorporation. According to NMR analysis the CHD/ethylene copolymerization is highly regioselective, accounting for exclusive formation of 1,4-cyclohexene units randomly distributed in the polyethylene backbone. Unfortunately, the molecular

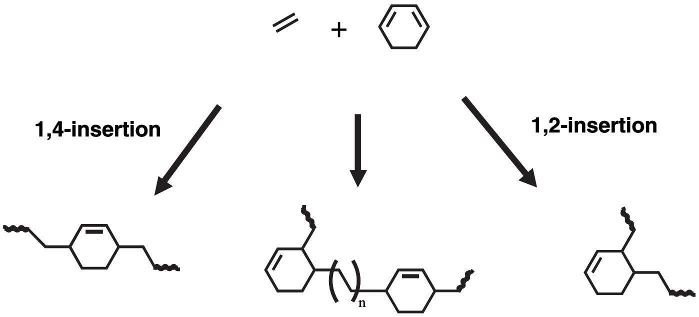

Figure 2.
Possible isomers resulting from 1,2-, 1,4- and mixed 1,2/1,4- insertion in CHD/ethylene copolymerization.

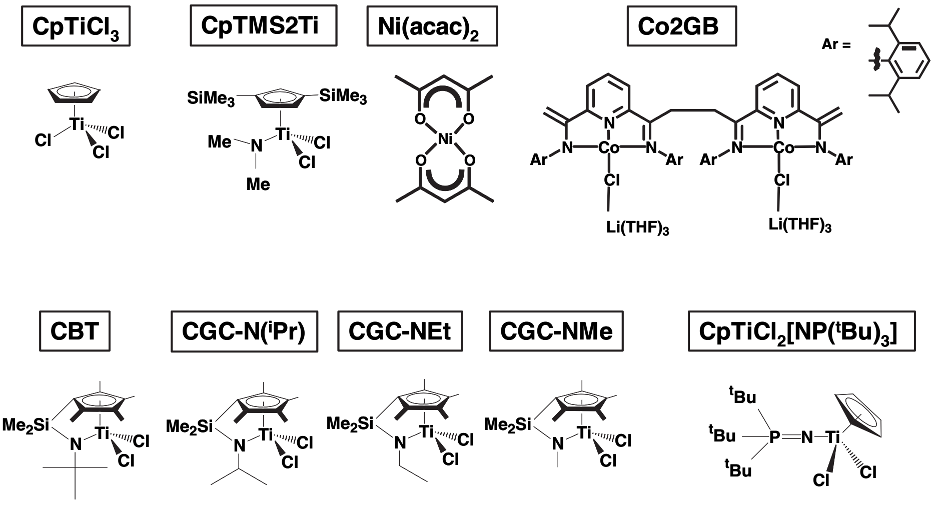

Figure 3.
Conventional and novel early and late transition metal complexes for the catalyst screening in CHD/ethylene copolymerization.

weight of such ethylene copolymers decreases with increasing CHD incorporation. CHD-rich ethylene copolymers gave molecular weights $M_n < 30{,}000$ g/mol.[6]

In order to improve activity, molecular weight and CHD incorporation in catalytic CHD/ethylene copolymerization various single-site catalysts were investigated (Figure 3). The family of titanium half-sandwich catalyst includes constrained geometry catalysts (CBT, CGC-N(^{i}Pr), CGC-NEt, CGC-NMe),[7] the highly active phosphinimide complex CpTiCl$_2$[N=P(^{t}Bu)$_3$][8] and the non-bridged titanium complexes CpTMS2Ti and CpTiCl$_3$. In addition a dinuclear cobalt(I) postmetallocene (Co2GB)[9] and Ni(acac)$_2$ were evaluated. Polymerization conditions are listed in Table 1.

Results of Catalyst Screening

The results of the catalyst screening in CHD/ethylene copolymerization are displayed in Figure 4. The screening was performed using the High Output Polymerization Screening (HOPS) tool.[10] The MAO-activated cobalt-based post-metallocene Co2GB showed the highest activity in the screening, but produced exclusively polyethylene. In contrast, Ni(acac)$_2$/MAO gave pure polycyclohexadiene in high yields. MAO-activated CpTiCl$_3$ CpTMS2Ti and CGC-N(^{i}Pr) gave copolymers in low yields. Moderate activities were observed for CGC-NMe/MAO and CGC-NEt/MAO. The highest activity to form copolymers was found for CpTiCl$_2$[NP(^{t}Bu)$_3$] and exceeds that of the

Table 1.
Polymerization conditions in 1,3-cycohexadiene/ethylene copolymerization. The experiments were carried out continually in a 200 mL Büchi Miniclave glass reactor, except the experiment for CpTiCl$_2$[N=P(^{t}Bu)$_3$].

solvent	toluene
polymerization temperature	60 °C[a)]
polymerization time	20 min[b)]
1,3-cyclohexadiene, c(CHD)	60 ml, 4.2 mol/L
total volume	150 mL
Al/Mt	
- Mt = Ti, Co	1000
- Mt = Ni	100
ethlylene pressure	5 bar[a)]
catalyst concentration	
- titanium catalysts	200 μmol/L
- Ni(acac)$_2$	737 μmol/L
- Co2GB	45 μmol/L
- CpTiCl$_2$[N=P(^{t}Bu)$_3$]	126 μmol/L

[a)] Modified conditions for CpTiCl$_2$[N=P(^{t}Bu)$_3$] : The reaction was performed in a semi-automated and temperature controlled 500 mL steel autoclave at T = 30 °C and p = 1 bar.

[b)] Polymerization with CBT/MAO quenched after 10 min for high viscosity of the reaction mixture.

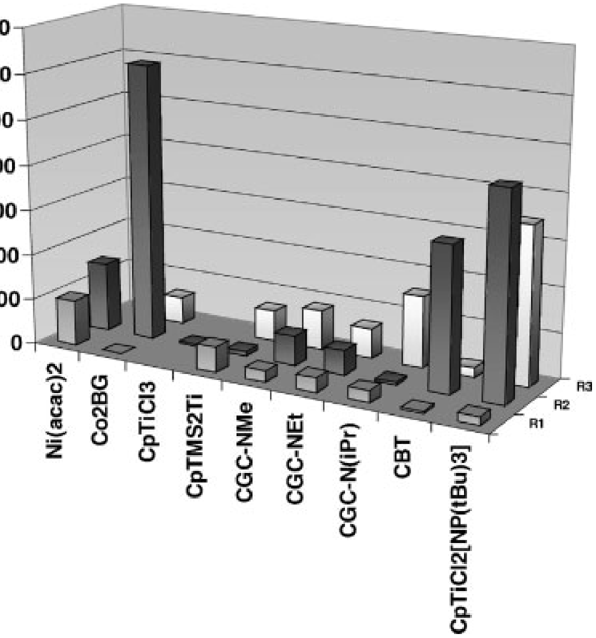

Figure 4.
Results of catalyst screening: R1: CHD incorporation [mol-%]; R2: catalyst activity [kg polymer/(mol/L olefin concentration * mol metal * h polymerization time); R3: molecular weight M_n [kg/mol]. Activity for $Ni(acac)_2$ was calculated as kg $_{PCHD}$/mol$_{Ni}$ · h . Activity for Co2GB was calculated as kg $_{PE}$/ mol$_{Co}$ · h · mol/L ethylene.

highly active constrained geometry catalyst CBT.

In contrast to CBT, however, the copolymers produced with the modified CGC catalysts exhibited much higher molecuar weights ranging from $M_n = 66{,}000$ to 156,000 kg/mol. The highest molecular weight for CHD/ethylene copolymers was achieved with the phosphinimide complex with up to $M_n = 347\,400$ g/mol.

CHD/Ethylene Copolymer Properties and Microstructure

The obtained CHD/ethylene copolymers are semicristalline or amorphous, depending on the amount of CHD incorporation. As reported in literature,[6] the semicristalline ethylene copolymer synthesized with CBT/MAO contains 5 mol-% CHD. With CHD incorporation exceeding 16 mol-% the copolymers are rendered amorphous.

The CHD incorporation of copolymers prepared via MAO activated CGC-NR (R = Me, Et, ^{i}Pr) varied between 25–31 mol-%. With the phosphinimide complex up to 17 mol-% CHD were incorporated into the polyethylene backbone. However, the highest CHD incorporation was achieved with CpTMS2/MAO and is as high as 56 mol-%.

Microstructure analysis was accomplished on the basis of ^{1}H NMR investigations (Figure 5). As already pointed out for CBT the titanium phosphinimide catalyst, and to a less degree CGC-NMe and CGC-NEt, account for 1,4-CHD insertion polymerization. CHD/ethylene copolymers comprising exclusively 1,4-enchained cyclohexene units show only one sharp peak for the olefinic protons at $\delta = 5.59$ ppm.[5,6]

Conclusion

In the catalyst screening CBT and $CpTiCl_2[N{=}P(^tBu)_3]$ exhibit the highest activities in CHD/ethylene copolymerization when using MAO as activator. Co2GB/MAO only yielded polyethylene. The phosphinimide based catalyst was outstanding with respect to the attractive combination of

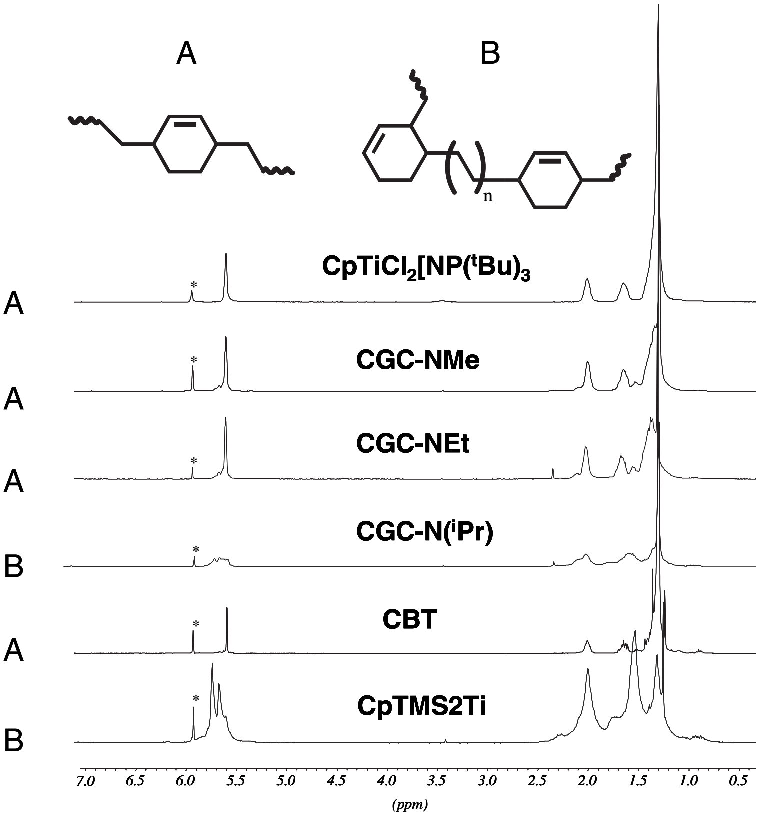

Figure 5.
^{1}H NMR spectra (300 MHz, $C_2D_2Cl_4$) of CHD/ethylene copolymers at $T = 120$ °C. The solvent peak is marked with an asterisk. For reasons of clarity the signals at $\delta = 1.31$ ppm (backbone methylene groups) are not completely displayed.

highly 1,4-regioselective CHD incorporation, high activity, and high molecular weight. The subsequent hydrogenation of poly(CHD-co-ethylene) represents a synthetic route to high molecular weight regioregular polyolefins containing 1,4-cyclohexene units in the backbone. Conversion of the olefin groups in the polymer backbone affords functionalized COCs.

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