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Synthesis by metallocene/MAO catalyst and functionalization of poly(ethene-*co*-4-vinylcyclohexene)

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Summary

New functional copolymers consisting of ethene and 4-vinylcyclohexene (4-VCH) were synthesized by a stereorigid metallocene / methylalumoxane catalyst. The content of 4-VCH depends on the polymerization temperature, thus influencing the polymeric properties. Investigations of the microstructure were made using ^{13}C NMR spectroscopy, thus revealing that 4-VCH is inserted regioselectively into the growing polymer chain. Hydroboration of selected copolymers followed by an oxidative workup yielded polyalcohols which display different polymeric properties than the precursor

Introduction

During the last years, chemical modification of polyolefins which aims at enhancing their chemical and physical properties, has become the goal of many investigations in the field of metallocene and Ziegler-Natta catalysis (1),(2),(3).

The synthesis of a chemically modified copolymer requires at least the incorporation of one monomer bearing a functional group. Conventional Ziegler-Natta catalysts as well as metallocene/MAO catalysts are very sensitive to functional monomers due to the formation of stable complexes between the catalyst and the monomer, which in turn extinguishes polymerization activity (4).

The reaction between the active catalyst site and the monomer is avoided by blocking the functional group with sterically demanding substituents (5). Another strategy is the copolymerization of α–olefins and nonconjugated diene monomers which do not interfere with polymerization. Conversion of all remaining double bonds delivers functional polymers (6),(7). Generally speaking, the incorporation rate of the copolymerization of nonconjugated linear diene monomer with ethene or propene is rather low and on the other hand most diene monomers are rather expensive (8).

The aim of this work was to prepare copolymers bearing a functional group using a cheap and easy-to-functionalize diene comonomer and to enhance the incorporation rate of the comonomer by choosing an appropriate metallocene/MAO system for the ethene diene monomer copolymerization. Therefore, we selected 4-vinylcyclohexene as comonomer and $Ph_2C(CpFlu)ZrCl_2$/MAO as the catalytic system which was found to be one of the most active systems for the copolymerization of ethene and cycloolefins (9).

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Experimental part

Materials:

4-VCH from Fluka was stirred with Triisobutylaluminium (TIBA, Witco) at ambient temperature for 72 h and distilled prior to use. Ethene was purchased from Linde Gas and purified by passing through columns containing mol sieve (4 Å) to remove traces of moisture and BASF catalyst RS 11 to remove polar impurities.

$Ph_2C(CpFlu)ZrCl_2$ was kindly donated by the Hoechst AG. Methylalumoxane (MAO) was obtained from Witco GmbH (Bergkamen). 9-borabicyclononane (9-BBN) was supplied by Aldrich as a 0.5 M solution in Tetrahydrofurane (THF). Toluene was dried over Na/K alloy and distilled before use. All reaction steps were carried out under an argon atmosphere using Schlenk techniques.

Polymerizations:

The polymerization reactions were performed in a 1l Büchi glass autoclave equipped with a stirrer bar. Prior to the polymerization, the autoclave was heated at 95 °C for 2 h and purged 5 times with argon. Toluene and the appropriate amount of 4-VCH were placed in the glass reactor. MAO solution was added by means of a syringe and the desired ethene pressure was adjusted. After 30 minutes the polymerization was started by injecting the prereacted metallocene/MAO catalyst solution. The polymerizations were quenched by adding a mixture of ethanol and aqueous KOH solution. The resulting polymer was stirred with ethanol/KOH solution for 12 h and washed thoroughly with water. All polymer samples were dried in vacuum at 40 °C for 12 h. Each polymerization was repeated three times to ensure reproducibility.

Functionalization of the copolymers:

The introduction of a hydroxy group was carried out according to following scheme: 2 g of copolymer (4-VCH content: 8 mol-%) were placed in a three necked flask equipped with a reflux condenser and a dropping funnel. The polymer was suspended in 80 ml toluene and 20 ml THF while heating up to 50 °C. Then, a solution of 31 ml 9-BBN (0.5M) in THF was added dropwise over a period of 10 minutes. After 3 h stirring at 65°C 40 ml NaOH solution (1.5 M) were added followed by a solution of 5 ml 30-% H_2O_2 in 60 ml THF. The reaction slurry was filtered and refluxed for 3 h with 250 ml methanol. After washing with methanol and drying at 40°C in vacuo the pendant polyalcohol was obtained.

Analytical methods:

The microstructure and incorporation rate of the copolymers were determined by ^{13}C-NMR-spectroscopy at 100 °C. The spectra were recorded on a Bruker MSL 300 spectrometer operating at 75.48 Mhz, resp. on a Bruker AM 360 operating at 90.4 MHz for the APT-spectra. The NMR samples were prepared by dissolving 200 mg copolymer in a mixture of tetrachloroethane and tetrachloroethane-d_2 (volume ratio 5:1). Molecular weights were measured by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 135 °C using a Waters 150-C gel permeation chromatograph equipped with four styragel HT columns (10^6, 10^5, 10^4 and 10^3 Å pore diameter). Cross fractionation chromatography (CFC) was performed using a Mitsubishi Petrochemical CFC T-150A equipped with an infrared detector. The polymer samples (150 mg) were eluted at different temperatures starting from 0 to 140°C with *o*-dichlorobenzene. Melting points (2nd Heat) and glass transition temperatures were determined using a Perkin Elmer DSC 4 instrument. All measurements were performed with a heating rate of 20 °C/min.

Results and discussion

Influence of the polymerization temperature:

All polymerizations were carried out under a defined set of experimental parameters. Except for the polymerization temperature, all other values were left constant. The polymerization temperature ranged from 0 to 60 °C and was varied in 15 °C steps. Table 1 displays the results of the polymerization performed at different polymerization temperatures:

Table 1: Polymerization results: amount of zirconocene = $5*10^{-6}$ mol; Al/Zr = 3000; [4-VCH] = 1.0 mol/l; [ethene] = 0.1 mol/l; reaction volume = 100ml

Sample No.	Polymerization temperature [°C]	Activity [kg /mol Zr*h]	Incorporation rate [%]	T_m / T_g [°C]	Mn*10^3 [g/mol]	Mw/Mn
1	0	10	33	n.d. / -15	29.7	2.06
2	15	56	17	58 / -17	31.9	1.96
3	30	195	8	80 / -12	29.4	1.86
4	45	474	5	96 / n.d.	30.7	1.79
5	60	705	4	104 / n.d.	28.4	1.84

The incorporation rate of 4-VCH is strongly dependent on the polymerization temperature and ranges from 4 to 33 mol-%. At higher temperatures, the incorporation level of 4-VCH is diminished compared to the copolymers synthesized at lower polymerization temperatures. The different incorporation rates can best be explained by considering the different rate constants of the monomers during insertion into a Zr-C-σ bond. Thus, ethene inserts faster into the growing polymer chain at higher polymerization temperatures.

4-VCH as a sterically demanding monomer has a diminished insertion rate compared to ethene. At lower polymerization temperatures, the ratio of the rate constants is turned in favor of 4-VCH, which results in the formation of copolymers with a high content of 4-VCH. A similar polymerization behaviour is observed for copolymerizations of ethene and hexene with Cp_2ZrCl_2 / MAO (10).

Due to different incorporation rates, the polymer samples are distinct from each other in their properties. The bulky cyclohexene moiety prevents a regular arrangement of the polymer chains which leads to decreased melting points and crystallinities of the copolymer compared to the ethene homopolymer (T_m = 138.0 °C). Samples with high 4-VCH contents display elastomeric properties.

Surprisingly, the influence of the polymerization temperature on the molecular weight is rather low. Compared to the ethene homopolymer ($M\eta$ = $630*10^3$ g/mol), lowered molecular weights are typical for copolymers which contain nonconjugated dienes (7).

Generally, the probability of a β-hydride elimination resp. a β-hydride transfer after the insertion of a 4-VCH unit in the growing chain to a 4-VCH monomer could be enlarged, which results in a more likely termination of the growing chain, thus explaining the low molecular weights. Also, the temperature invariance of the molecular weight can be explained by considering the different incorporation rates of 4-VCH in the copolymer samples and the preferred chain termination after the insertion of a 4-VCH unit. At elevated polymerization temperatures, the incorporation rate of 4-VCH into the growing polymer chain is comparatively low and the rate of a general β-hydride elimination resp.

transfer to a monomer is rather high, resulting in the formation of polymer chains with low molecular weight. The rate of chain terminating steps is small at low polymerization temperatures, but the incorporation rate of 4-VCH is increased. Taking into account, that the chain terminating step occurs preferably after the insertion of a 4-VCH unit, these two antagonistic effects compensate each other, thus leveling out a possible temperature dependency.

The polydispersity Mw/Mn of the ethene-VCH copolymers ranges between 1.8 and 2.1, according to the proposed single site character of metallocene catalysts. No polymer blends but real copolymers are obtained, which is further confirmed by cross fractionation chromatography (CFC) (11). The polymer samples are uniform and can not be split up into different fractions.

The activity is proportional to the polymerization temperature and is diminished at lower polymerization temperatures.

Microstructure of Ethene-(4-VCH) copolymers:

The ^{13}C-NMR spectrum of a copolymer sample prepared at 60 °C (4-VCH content: 4 mol-%) is shown in fig. 1:

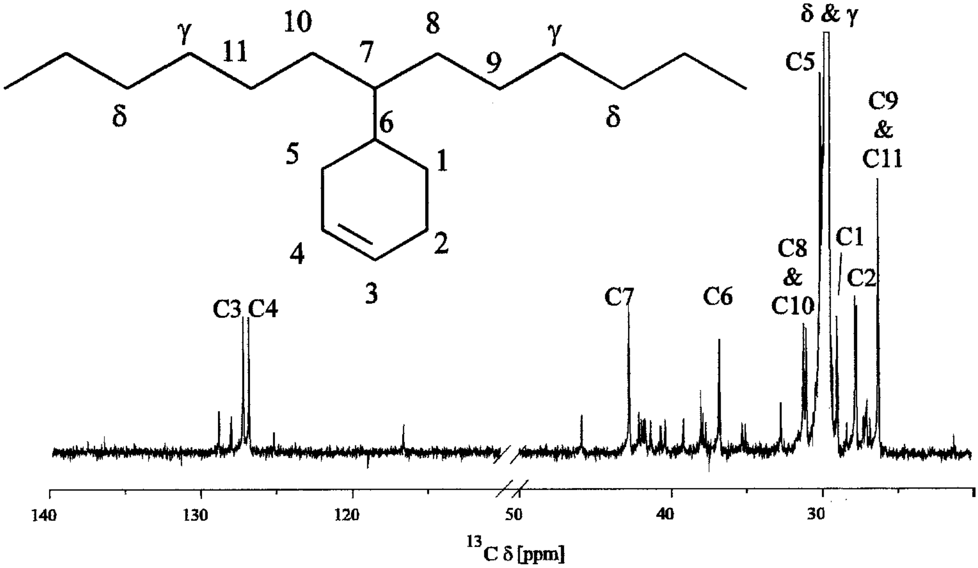

Figure 1: ^{13}C NMR spectrum of sample 5 prepared at 60 °C.

The peak assignments of the EVE-triad have been achieved by comparison of the experimental values with those calculated by using the SPECAL© Software available in the SPECINFO© Database (12) and the method of Lindeman and Adams (13).

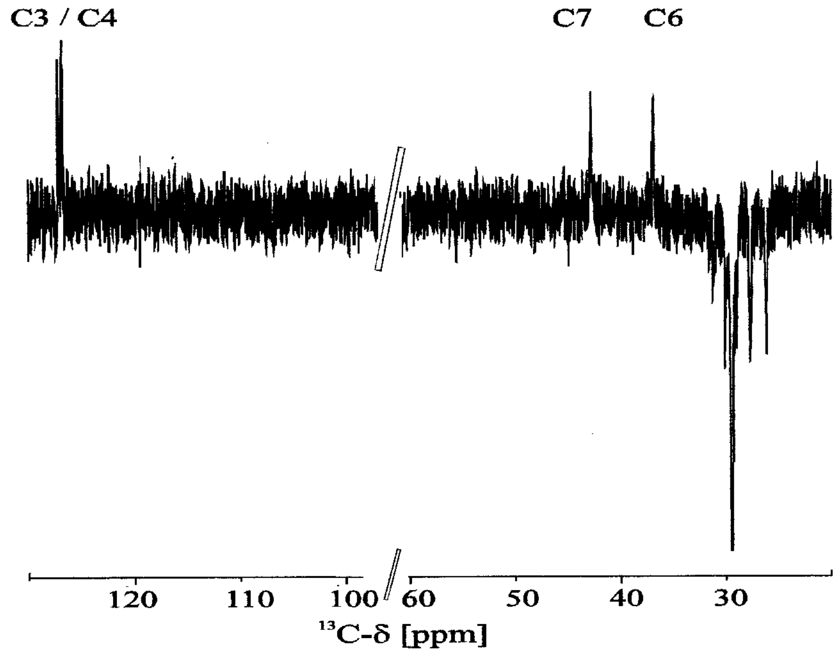

Figure 2: ^{13}C APT NMR spectrum of sample 5 prepared at 60 °C.

The investigation of the APT-spectrum (fig.2) indicates the existence of four methine carbons at 127.29, 126.91, 42.74 and 36.89 ppm. The last two peaks have been assigned to the branching methine carbon (C7) and the methine carbon (C6) in the cyclohexenyl ring, respectively. The remaining methine carbons are attached to the double bond of the cyclohexene fragment. The ^{13}C chemical shifts of the signals for the double bond give clear evidence, that only the vinyl double bond, and not the endocyclic double bond has reacted in the course of polymerization, because of the lack of signals at 143.7 resp. 112.89 ppm, which would mark the exocyclic vinyl double bond. Thus, the assignments for an isolated 4-VCH unit (represented by the triad EVE) have been made according to table 2.:

Table 2 : Assignment of ^{13}C-NMR chemical shifts in ethene-(4-VCH) copolymers

Carbon No.	1	2	3	4	5	6	7	8 / 10	9 / 11
^{13}C δ [ppm]	28.89	27.64 27.70	127.29	126.91	30.01	36.73	42.69	30.94 31.12	26.16

It should be noted that the microstructure of ethene-(4-VCH) copolymers is found to be complicated due to the existence of diastereomeric units which are formed by the stereospecific insertion of the *R*- and *S*-enantiomer of 4-VCH (14), resulting in a signal split for the carbons C2 and C11 / C18. The remaining weak signals are originated by endgroups and small blocks of 4-VCH.

Functionalization of ethene-(4-VCH) copolymers

The functionalization was carried out using a convenient route via the formation of the borane adduct, followed by oxidative cleavage which renders the correspondent polyalcohol (7), (15).

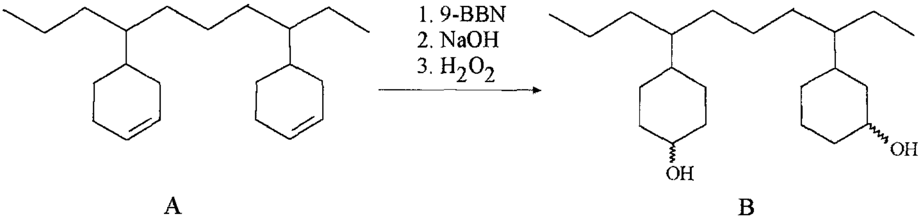

Figure 3: Reaction scheme for the conversion of ethene-(4-VCH) copolymers into the pendant polyalcohols

By comparing the ^{13}C NMR spectra of the polymer sample before and after the hydroboration reaction (fig. 4), it is evident due to the lack of peaks in the range of 130 to 120 ppm that the conversion into a hydroxy group is quantitative. Concurrently, the formation of four new signals at 71.29, 71.08, 66.97 and 66.51 could be observed.

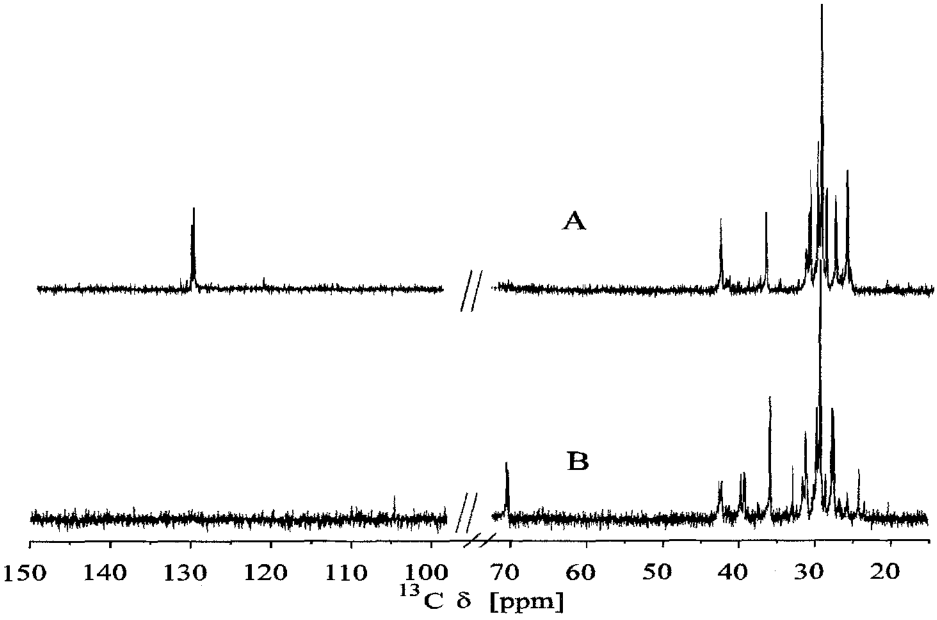

Figure 4: NMR spectra of sample 1 before (A) and after hydroboration (B)

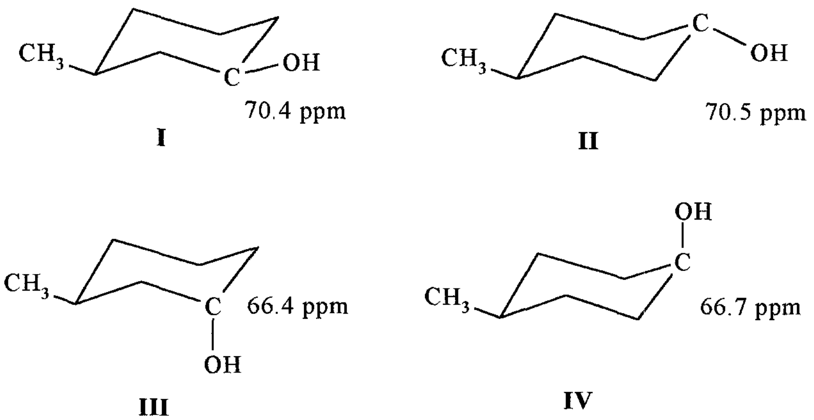

Figure 5: Structure and ^{13}C chemical shifts of model compounds **I-IV** for all possible hydroboration reaction products

The observed signals are in good agreement with ^{13}C-NMR chemical shifts for the model compounds of possible reaction products depicted in fig.5. Hence, we concluded that the hydroboration reaction of the cyclohexene double bond in the copolymer is neither perfectly regioselective.nor stereoselective, leading to a variety of possible diastereomeric products. The molecularweight and the polydispersity of the polyalcohol have not been changed significantly by the functionalization reaction. The thermal behavior of the new polyalcohols differs from the corresponding precursor. In case of sample 1 the glass transition temperature is raised and a melting point was detectable.

Table 3: Polymeric properties of a selected ethene-(4-VCH) copolymer

Sample No.	Status	Tm [°C]	Tg [°C]	Mn*10^3 [g/mol]	Mw/Mn [ ]
1	precursor	n.d.[1.)]	-15	29.7	2.06
1-OH	product	60	-2	25.0	1.86

[1.)] n.d. = not detectable

These results can be interpreted by hydrogen bond interaction, which are caused by the formed hydroxy groups attached to the cyclohexyl moiety.

Conclusion

4-Vinylcyclohexene and ethene can be copolymerized by catalysis with the c_s-symmetric metallocene $Ph_2C(CpFlu)ZrCl_2$ in combination with MAO. The active species is well suited for the incorporation of bulky diene monomers like 4-VCH. Variation of the incorporation rate of 4-VCH can be achieved by changing the polymerization temperature. This leads to incorporation rates ranging from 4 to 33 mol-%. Hence, the prepared copolymers display different properties depending on their content of 4-VCH. In addition, NMR-investigations using different pulse techniques delivered plausible assignments of the observed NMR signals to the microstructure of the copolymers. The proposed mechanism of termination can explain the low molecular weight of the copolymers compared to an ethene homopolymer prepared with the same metallocene catalyst system under similar conditions. Functionalization of ethene-(4-VCH) copolymers can be achieved by hydroboration and oxidative work-up, which leads to polymers containing hydroxy groups at the cyclohexyl ring. Metallocene/MAO catalysts can thus act as a tool for preparing well defined, tailored functional polymers. These new polymers could be interesting precursors for the synthesis of compatibilizers or adhesives (1), (16). In addition, the new functionalized copolymers are very promising support materials for immobilized catalysts which is currently under investigation.

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