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COPOLYMERIZATIONS OF OXYGEN-FUNCTIONALIZED OLEFINS WITH PROPYLENE USING METALLOCENE/METHYLALUMINOXANE CATALYST

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Abstract—Nine oxygen-functionalized olefins were copolymerized with propylene by using a homogeneous $Et(Ind)_2ZrCl_2$ catalyst activated with methylaluminoxane (MAO). In addition to alcohols, comonomers containing acid or ester functionalities could also be copolymerized. The structure of the comonomer had a marked effect on its polymerizability and on the deactivation of the catalyst. The longer the spacer group the better the incorporation of the comonomer. The highest comonomer content of polymer (2.7 wt%) was achieved with 10-undecen-1-ol and the highest conversion (12.1%) with 10-undecenoic acid. Steric protection of the functional group diminished the deactivating influence of the comonomer. The comonomers containing keto or weakly shielded ester groups poisoned the catalyst most. Incorporation of functional comonomer was accompanied by a decrease in the melting temperature of the polymer. The molar masses of the copolymers were slightly lower than the molar mass of the propylene homopolymer and the molar mass distributions of all copolymers were narrow.
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INTRODUCTION

The lack of reactive groups in polyolefins significantly limits their use. Incorporation of functional groups into the hydrocarbon backbone gives polymers with improved adhesion, dyeability, permeability and compatibility properties. However, direct polymerization of functional monomers in Ziegler–Natta processes is not possible because of catalyst poisoning by Lewis base components [1].

A number of approaches have been described [1] to minimize the undesirable interaction between catalyst components and functional groups. The preferred methods are insulation of the double bond from the heteroatom by a spacer group, increase of the steric hindrance about the heteroatom, and decrease of the electron donating character of the heteroatom via attachment of electron withdrawing substituents on or adjacent to it. There are few examples in the older literature of attempts to polymerize monomers containing functional groups with Ziegler–Natta catalysts [2, 3].

The appearance of metallocene catalysts has excited new interest in polyolefin functionalization by coordination catalysts. Chung has investigated the borane-containing functional monomers in olefin copolymerization using homogeneous metallocene catalysts [4]. A new approach to end-functionalized polypropylenes has been studied by Mülhaupt *et al.* [5] and Shiono *et al.* [6, 7]. And yet another approach is the metallocene-catalyzed preparation of polyolefin with pendant unsaturation,

and subsequent functionalization of it by hydroboration or epoxidation [8, 9]. Recently, direct homo- and copolymerizations of α-olefin monomers containing protected alcohol, amine or phenol groups have been described [10, 11].

Earlier studies by our group have demonstrated that 10-undecen-1-ol can be directly copolymerized with ethylene or propylene by using soluble metallocene/methylaluminoxane (MAO) catalysts [12–14]. In the present study we investigated the suitability of various oxygen-functionalized monomers for copolymerization with propylene using bridged zirconocene as catalyst. Results of chemical analyses of the copolymers are presented.

EXPERIMENTAL

Chemicals

The *rac*-ethylene-bis(1-indenyl)zirconium dichloride $(Et(Ind)_2ZrCl_2)$ catalyst and methylaluminoxane (MAO, a 10 wt% solution in toluene, $M = 1000$ g/mol) were obtained from Witco GmbH and used as received. 10-Undecen-1-ol (96%), 5-hexen-1-ol (>97%), 2-methyl-3-buten-2-ol (>97%) and 10-undecenoic acid (97%) were purchased from Fluka. Methyl 9-decenoate was synthesized by Neste. The comonomers were further purified with molecular sieves (3 Å) and purged with nitrogen before use. Toluene (GR grade from Merck) and propylene (grade 2.8 from AGA) were purified by passing them through columns filled with molecular sieves, BASF R3-11 catalyst and activated Al_2O_3.

Syntheses of functional comonomers

Besides the commercially available comonomers, four different oxygen-functional long-chain alkenes were syn-

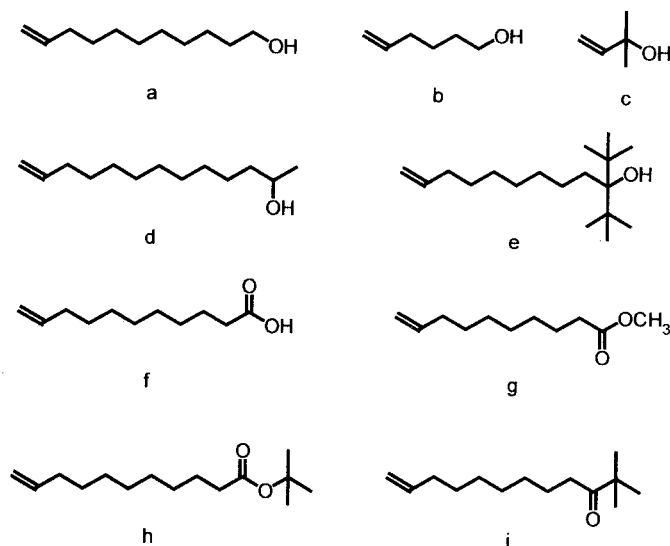*To whom all correspondence should be addressed.

Fig. 1. Structures of the functional monomers used in the copolymerizations: (a) 10-undecen-1-ol, (b) 5-hexen-1-ol, (c) 2-methyl-3-buten-2-ol, (d) 12-tridecen-2-ol, (e) 2,2-dimethyl-3-(1,1-dimethylethyl)-11-dodecen-3-ol, (f) 10-undecenoic acid, (g) methyl 9-decenoate, (h) *tert*-butyl 10-undecenoate, (i) 2,2-dimethyl-11-dodecen-3-one.

thesized. 12-Tridecen-2-ol (Fig. 1(d)) and 2,2-dimethyl-3-(1,1-dimethylethyl)-11-dodecen-3-ol (Fig. 1(e)) were synthesized via Grignard-type reactions and along with the latter alcohol 2,2-dimethyl-11-dodecen-3-one (Fig. 1(i)) was isolated and characterized as a reaction product. *Tert*-butyl 10-undecenoate (Fig. 1(h)) was synthesized from 10-undecenoic acid and *tert*-butanol. The full details of the syntheses will be published elsewhere.

Apparatus and method of polymerization

Polymerizations were carried out in toluene in a 0.5 dm³ stainless steel reactor equipped with a propeller-like stirrer. The stirring speed was 400 rpm, temperature 30°C and partial pressure of propylene 3.0 bar. Et(Ind)$_2$ZrCl$_2$ was used as catalyst and MAO as cocatalyst. The amount of catalyst in one polymerization was 2.0 mg (4.8 × 10^{-6} mol) and the Al/Zr molar ratio was 4000.

Toluene (300 cm³) was introduced to the nitrogen-purged reactor. The cocatalyst solution and the comonomer were added to the reactor under nitrogen pressure. The reactor temperature was controlled by circulating water in the reactor jacket. The propylene feed was started at the polymerization temperature and after the equilibrium had been reached (about 30 min) polymerization was initiated by pumping the toluene solution of the catalyst into the reactor. During polymerization the partial pressure of propylene was maintained constant with an electronic pressure controller.

After the polymerization time of 60 min the reactor was degassed and the product was precipitated with dilute hydrochloric acid solution in ethanol. The polymer was isolated by filtering, washed with ethanol and dried under vacuum.

Polymer characterization

A Waters 150-C ALC/GPC gel permeation chromatograph operating at 140°C and equipped with three Polymer Laboratories PLgel columns and an RI detector was used to determine the molar masses and the molar mass distributions of the polymers. Solvent 1,2,4-trichlorobenzene was applied at a flow rate of 1.0 cm³/min. The

columns were universally calibrated with narrow molar mass distribution polystyrene standards.

The melting temperatures were recorded with a Perkin Elmer DSC-7 differential scanning calorimeter. Indium was used for the calibration of the temperature scale. The melting endotherms were measured upon reheating of the polymer sample to 160°C at a heating rate of 10°C/min.

The NMR spectra of the copolymers were recorded at 120°C or 130°C with a Jeol GSX 400 NMR spectrometer from samples dissolved in 1,1,2,2-tetrachloroethane-d$_2$. The comonomer contents were calculated from the ^{1}H NMR spectra. FTIR spectra were measured with a Nicolet 750 Magna FTIR spectrometer from melt-pressed thin polymer films.

RESULTS AND DISCUSSION

The structures of the nine functional-group-containing compounds are presented in Fig. 1. These comonomers were copolymerized with propylene in the presence of the bridged metallocene catalyst Et(Ind)$_2$ZrCl$_2$ and cocatalyst methylaluminoxane (MAO). The reaction conditions and the results of the polymerizations are set out in Tables 1 and 2.

Effect of the comonomer structure on the activity of the catalyst

The comonomers differed from each other in the type of functional group (alcohol, acid, ester and ketone), in the length of spacer between the functional group and the polymerizable double bond and in the steric hindrance of the oxygen-containing group. The copolymerization series were performed by varying the concentration of the functional comonomer in the feed and keeping other conditions constant. All the comonomers caused a significant decrease in the polymerization activity

Table 1. Results of copolymerizations between propylene and hydroxyl-group-containing monomers in toluene with $Et(Ind)_2ZrCl_2/MAO$ catalyst system. Polymerization conditions: $T_p = 30°C$, $p_{C_3H_6} = 3.0$ bar, $Al/Zr = 4000$ mol/mol, $t_p = 60$ min

Run	Comonomer	$c_{comonomer}$ (mmol/l)	Yield (g)	Activity (kg P/ mol Zr·h)	M_w (g/mol)	M_w/M_n	T_m (°C)[a]
1	–	–	79.3	16,600	33,500	1.8	138.2
2	10-undecen-1-ol	3.3	12.4	2600	35,000	1.7	136.6
3	10-undecen-1-ol	10.0	3.8	800	28,300	1.7	134.3
4	10-undecen-1-ol	16.7	0.5	110	28,200	1.7	130.6
5	5-hexen-1-ol	3.3	18.7	3900	30,500	2.1	136.7
6	5-hexen-1-ol	10.0	5.4	1100	25,200	2.1	136.4
7	5-hexen-1-ol	17.0	0.9	180	20,500	2.0	133.9
8	12-tridecen-2-ol	3.3	12.6	2600	35,000	1.7	137.4
9	12-tridecen-2-ol	6.7	2.7	570	29,500	1.7	134.0
10	12-tridecen-2-ol	10.0	2.4	510	28,000	1.8	132.5
11	2-methyl-3-buten-2-ol	3.3	41.0	8600	32,200	2.0	137.0
12	2-methyl-3-buten-2-ol	10.0	12.6	2600	29,900	2.0	136.4
13	2-methyl-3-buten-2-ol	19.0	3.2	670	31,400	2.0	135.9
14	2,2-dimethyl-3-(1,1-dimethylethyl)-11-dodecen-3-ol	6.7	15.1	3200	32,900	1.8	136.0

[a]Heating rate 10°C/min.

compared with the homopolymerization of propylene. The effect on activity also intensified when the concentration of comonomer was increased.

The deactivation of the catalyst is due to the interactions between the Lewis acid catalyst components and the free electron pairs of oxygen atoms in the comonomer structures. It can be assumed that the interaction will be weakened if the oxygen atom is shielded by substituents added to the adjacent carbon atom. The significance of shielding is clearly evident from Fig. 2, where the effect of different types of alcohol comonomers on the activity of the catalyst is compared. As can be seen, the primary and secondary alcohols are more detrimental to the catalyst than the tertiary ones. The similar deactivating action of 5-hexen-1-ol and 10-undecen-1-ol indicates that the influence of spacer length on the interaction between comonomer and catalyst components is insignificant.

Besides the alcohols, comonomers containing various carbonyl groups were tested in copolymerizations. The rate decreasing effect of 10-undecenoic acid on the polymerization was at the same level as for the corresponding alcohol, 10-undecen-1-ol. Of the two esters, the tert-butyl derivative was tolerated better than the methyl ester, evidently again due to the better protective effect of the bulkier

tert-butyl group. Of all the comonomers tested 2,2-dimethyl-11-dodecen-3-one was the most detrimental to the catalyst. The more intense catalyst poisoning effect of the keto and methyl ester groups than of the hydroxyl and acid groups might be connected with the role of MAO in the copolymerizations. As we have earlier suggested [13], the true comonomer in the case of alcohol comonomer probably is an alcoholate formed in the reaction between the comonomer and MAO. Possibly MAO is not as effective in preventing keto and ester groups from reacting with the catalyst.

Effect of comonomer structure on the polymerizability

The polymerizability of the functional comonomers was studied by determining the comonomer contents of the prepared copolymers by ^1H NMR spectroscopy. Some of the results are presented in Table 3. The highest comonomer content of copolymer, 0.7 mol%, was achieved when 10-undecen-1-ol was used as comonomer. With the same feed concentration the amount of 5-hexen-1-ol in the copolymer was only 0.3 mol%. Perhaps the lower reactivity of 5-hexen-1-ol is due to the shorter spacer length. When the distance between the double bond and the oxygen atom is short, the

Table 2. Results of copolymerizations between propylene and carbonyl-group-containing monomers in toluene with $Et(Ind)_2ZrCl_2/MAO$ catalyst system. Polymerization conditions: $T_p = 30°C$, $p_{C_3H_6} = 3.0$ bar, $Al/Zr = 4000$ mol/mol, $t_p = 60$ min

Run	Comonomer	$c_{comonomer}$ (mmol/l)	Yield (g)	Activity (kg P/ mol Zr·h)	M_w (g/mol)	M_w/M_n	T_m (°C)[a]
1	–	–	79.3	16,600	33,500	1.8	138.2
15	10-undecenoic acid	3.3	16.5	3500	32,100	1.9	137.4
16	10-undecenoic acid	6.7	5.4	1100	30,300	1.9	135.7
17	10-undecenoic acid	10.0	2.8	580	28,400	1.9	134.6
18	methyl 9-decenoate	1.7	7.7	1600	32,900	1.8	137.7
19	tert-butyl 10-undecenoate	3.3	11.3	2400	31,600	1.9	137.1
20	tert-butyl 10-undecenoate	6.7	5.4	1100	29,700	1.9	139.1
21	tert-butyl 10-undecenoate	10.0	1.6	340	25,400	1.8	133.2
22	2,2-dimethyl-11-dodecen-3-one	3.3	traces	<100	n.d.[b]	n.d.[b]	n.d.[b]

[a]Heating rate 10°C/min.
[b]Not determined.
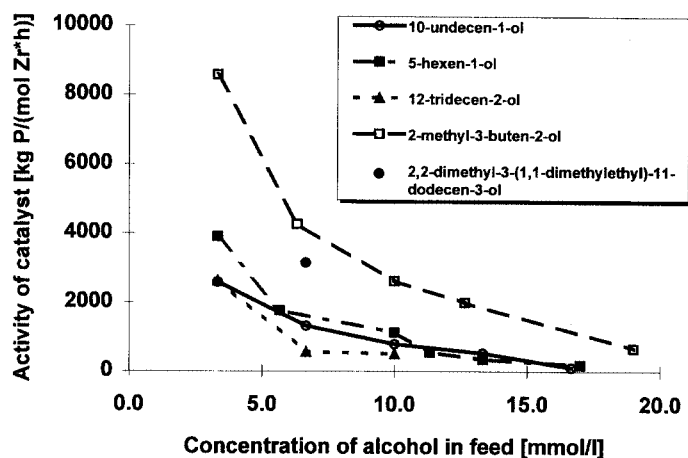
Fig. 2. Influence of the concentration and the type of alcohol on the activity of Et(Ind)$_2$ZrCl$_2$ catalyst in propylene copolymerizations. Polymerization conditions: $T_p = 30°C$, $p_{C_3H_6} = 3.0$ bar, Al/ Zr = 4000 mol/mol, $t_p = 60$ min.

bulky alcoholate group may shield the double bond and reduce its reactivity. Among the alcohols, 12-tridecen-2-ol was the most reactive in terms of conversion of the comonomer. 2-Methyl-3-buten-2-ol did not copolymerize at all, evidently because the two methyl branches next to the vinyl group hinder the coordination of the double bond to the catalyst center.

The amount of carbonyl-group-containing monomer in the copolymer was estimated from melt-pressed copolymer films by FTIR spectroscopy. The FTIR spectrum of poly(propene-co-10-undecenoic acid) containing 2.4 wt% functional units (by ^{1}H NMR) is presented in Fig. 3. The strong carbonyl absorption is clearly detectable. The conversions of 10-undecenoic acid and tert-butyl 10-undecenoate were higher than those of alcohol comonomers, and the incorporation of comonomers was at about the same level as with alcohol comonomers. This indicates that the type of functional group is not of great importance for the polymerizability of the comonomer if the spacer is long enough.

Effect of comonomer on the chemical properties of polymer

The weight-average molar mass (M_w) of propylene homopolymer was 33,500 g/mol. In most cases, addition of comonomer to the reaction mixture resulted in a drop in the molar mass of the poly-

mer. The most pronounced decrease was with 5-hexen-1-ol, and the M_w was 20,500 g/mol when the concentration of comonomer in the feed was 17.0 mmol/l. The lowering of molar mass with increasing comonomer content in the reaction mixture does not necessarily indicate incorporation of the comonomer but rather the ability of the comonomer to terminate the propagation of the polymer chain. The comonomers containing tertiary alcohol did not give rise to noticeable change in the molar mass of the polymer. No broadening of molar mass distributions was observed, in contrast to ethylene/functional monomer copolymerizations with non-bridged (n-BuCp)$_2$ZrCl$_2$ and (Ind)$_2$ZrCl$_2$ catalysts [12-14]. The melting temperatures of copolymers decreased along with the higher incorporation of the comonomer. Judging by the DSC measurements the copolymers still have only one melting transition.

CONCLUSIONS

Several different oxygen-functionalized olefins, including alcohols, acid and ester, could be copolymerized with propylene by using the metallocene/MAO catalyst system. The activity of the catalyst was always much lower in the copolymerizations than in the homopolymerization of propylene, how-

Table 3. Comonomer contents of differently functionalized polypropylenes prepared with the Et(Ind)$_2$ZrCl$_2$/MAO catalyst system. Polymerization conditions: $T_p = 30°C$, $p_{C_3H_6} = 3.0$ bar, Al/Zr = 4000 mol/mol, $t_p = 60$ min

| Run | Comonomer | $c_{comonomer}$ in feed (mmol/l) | Comonomer in polymer | | Conversion (%) |
			mol%	wt%	
4	10-undecen-1-ol	16.7	0.7	2.7	1.7
7	5-hexen-1-ol	17.0	0.3	0.6	1.0
10	12-tridecen-2-ol	10.0	0.3	1.3	5.3
13	2-methyl-3-buten-2-ol	19.0	0	0	0
16	10-undecenoic acid	6.7	0.2	0.7	10.2
17	10-undecenoic acid	10.0	0.6	2.4	12.1
21	tert-butyl 10-undecenoate	10.0	detectable[a]	detectable[a]	

[a]Because of the poor solubility, the comonomer content of polymer could not be determined quantitatively.
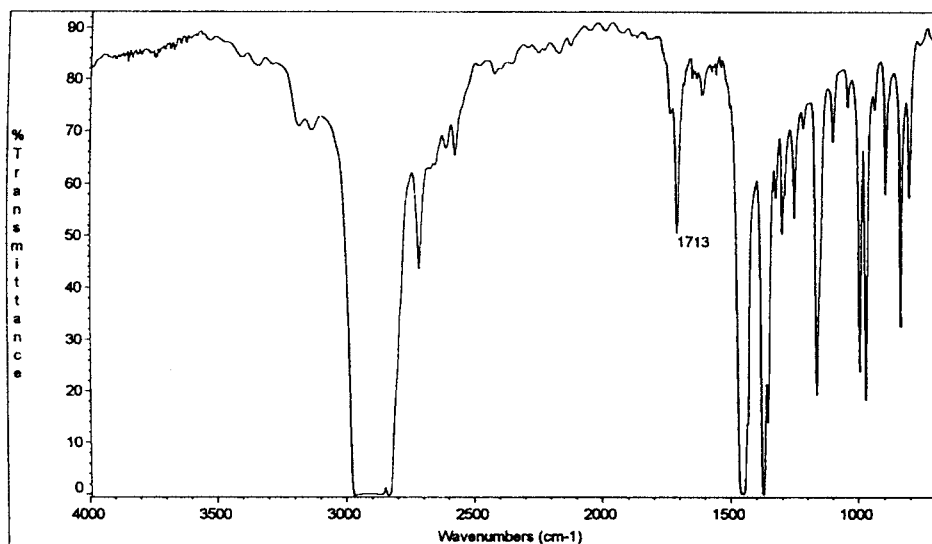
Fig. 3. FTIR spectrum of the copolymer of propylene and 10-undecenoic acid containing 2.4 wt% functional units.

ever. The structure of the comonomer affected both the copolymerizability and the magnitude of the deactivation of the catalyst. A long spacer between polymerizable double bond and the oxygen atom was observed to favor the copolymerizability of the functional comonomer. The steric protection around the functional group significantly diminished the negative effect on the polymerization rate. The catalyst poisoning was most intense with compounds containing keto or methyl ester groups. The molar masses of copolymers were lower than the molar mass of propylene homopolymer, but the molar mass distributions remained narrow.

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