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Synthesis of nitrogen-functionalized polyolefins with metallocene/methylaluminoxane catalysts

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Summary

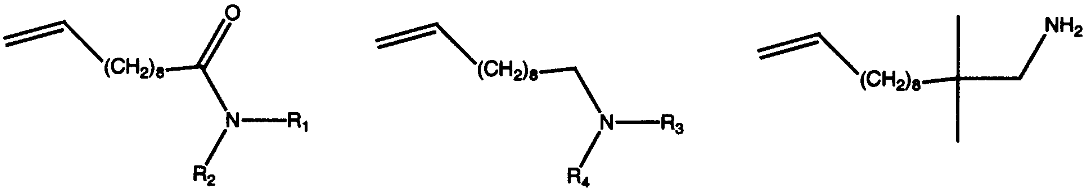
Thirteen differently substituted long-chain amide- and amine-functional alkenes were synthesised and used as comonomers in zirconocene/methylaluminoxane-catalysed copolymerizations with ethylene and propylene. Characterization of the prepared copolymers showed the formation of functionalized copolymers with isolated comonomer units. The incorporation level of the comonomers ranged from 0.24 to 1.3 mol % with ethylene and from 0.04 to 0.96 mol % with propylene. The molar masses of the copolymers were lower than those of the corresponding homopolymers. End group analysis of the copolymers by NMR suggested that the dominant chain termination mechanism was chain transfer to aluminium.

Introduction

Chemically modified, functionalized polyolefins form a polymer group of great commercial interest. The preparation of functionalized polyolefins can proceed either by chemical modification of preformed polyolefins or by copolymerization of functional, polar monomers with simple olefins [1]. While the copolymerization approach has been successfully utilized in high-pressure free-radical processes, controlled copolymerization of polar comonomers under mild conditions remains a challenge [1,2]. The most versatile catalysts for olefin polymerization, namely Ziegler-type catalysts, are oxophilic and easily lose their activity when Lewis basic comonomers are added.

Along with oxygen-functional monomers, nitrogen-functional vinylic comonomers are among the most widely studied functional comonomers in copolymerizations with ethylene, propylene or other α-olefins [2]. Giannini [3,4] found that unsaturated tertiary amines could be homopolymerized with Ziegler-Natta titanium catalysts provided that the nitrogen atom of the monomer was shielded by branched alkyl groups, and the distance of the amine functionality from the double bond was long enough. Waymouth et al. studied zirconocene/borate-catalysed homo- and copolymerizations of tertiary amine-functional olefins [5-7] as well as a sterically hindered alkoxyamine [8]. Hindered piperidine derivatives have been used as comonomers to improve the stability of polypropylene and polyethylene prepared with heterogeneous or homogeneous Ziegler-type catalysts [9,10]. The copolymerization of *N*,*N*-bis(trimethylsilyl)-amino-10-undecene with ethylene yielded, after acidic hydrolysis, polyethylene containing primary amino groups [11].

In earlier papers, we have described the metallocene-catalysed synthesis of functionalized polyethylenes and polypropylenes with hydroxyl, acid, ester or ether groups [12-16]. In the present study we extend the range of comonomers to vinyl-substituted amides and amines (Figure 1). Comparisons between differently substituted comonomers in the copolymerizations with ethylene and propylene are made in terms of catalyst activity and copolymer properties.



1 $R_1 = H, R_2 = Me$
2 $R_1 = H, R_2 =$ *tert*-Bu
3 $R_1 = R_2 = Me$
4 $R_1 = R_2 = Et$
5 $R_1 = R_2 =$ *i*-Pr

6 $R_3 = H, R_4 = Me$
7 $R_3 = H, R_4 =$ *tert*-Bu
8 $R_3 = R_4 =$ *i*-Pr
9 $R_3 = R_4 = H$
10 $R_3 = Bz, R_4 =$ *tert*-Bu
11 $R_3 = R_4 =$ *sec*-Bu
12 $R_3 = R_4 = Me$

13

Figure 1. **Nitrogen-functional comonomers: *N*-methyl-10-undecenamide (1), *N-tert*-butyl-10-undecenamide (2), *N,N*-dimethyl-10-undecenamide (3), *N,N*-diethyl-10-undecenamide (4), *N,N*-diisopropyl-10-undecenamide (5), *N*-methyl-10-undecenylamine (6), *N-tert*-butyl-10-undecenylamine (7), *N,N*-diisopropyl-10-undecenylamine (8), 10-undecenylamine (9), *N*-benzyl-*N-tert*-butyl-10-undecenylamine (10), *N,N*-di-*sec*-butyl-10-undecenylamine (11), *N,N*-dimethyl-10-undecenylamine (12), 2,2-dimethyl-11-dodecenylamine (13)**

Experimental

Chemicals

The metallocene catalysts *rac*-ethylenebis(1-indenyl)zirconium dichloride $[Et(Ind)_2ZrCl_2]$ and *rac*-dimethylsilylbis(2-methylindenyl)zirconium dichloride $[Me_2Si(2\text{-}MeInd)_2ZrCl_2]$ were obtained from Witco (Bergkamen, Germany) and Boulder Scientific Company (Mead, CO, USA), respectively. Methylaluminoxane (MAO, 10 wt % solution in toluene, total Al content 4.82 wt %, of which 35.7% as trimethylaluminium) was purchased from Witco and used as received. Toluene (GR grade, Merck, Darmstadt, Germany) was refluxed over Na/benzophenone and subsequently distilled under nitrogen. Ethylene (grade 3.5, Air Liquide, Liege, Belgium) and propylene (grade 3.5, Messer Griesheim, Krefeld, Germany) were further purified by being passed through columns filled with 3-Å, molecular sieves, BASF R3-11 copper catalyst and activated Al_2O_3.

Synthesis of functional comonomers

Amides **1** - **5** were prepared [17] from 10-undecenoyl chloride and $MeNH_2$ (40 % aq.), *tert*-$BuNH_2$, Me_2NH (40% aq.), Et_2NH or $(i\text{-}Pr)_2NH$. Reduction [17] of the amides **1**, **2** and **5** with $LiAlH_4$ in refluxing THF produced the amines **6** - **8**. Amines **9** - **11** were obtained analogously by reducing the amides $CH_2{=}CH(CH_2)_8CORR^1$ $(R,R^1{=}H;$

R=*tert*-Bu, R^1=Bz; or R=R^1=*sec*-Bu) prepared [17] from 10-undecenoyl chloride and NH_3 (25% aq.), *tert*-BuBzNH or (*sec*-Bu)$_2$NH. Amine **12** was prepared from 11-bromoundecene and Me_2NH (40% aq.) as previously described [18]. Amine **13** was synthesised via α-dialkylation [19] of 11-dodecenenitrile, prepared [20] from 10-undecen-1-ol, and reduction [21] of the obtained α-dimethylated product with $LiAlH_4$. All the crude products were purified by vacuum distillation and stored under molecular sieves.

Polymerization

The polymerization experiments were carried out in a 0.5- or 1.0-dm^3 stainless steel reactor (Büchi, Uster, Switzerland) equipped with a magnetically driven stirrer. The reactor was evacuated and flushed with nitrogen several times before the addition of toluene, MAO solution and comonomer. The mixture was stirred for 15 min, during which time the reaction mixture was saturated with the gaseous monomer. The polymerization was then initiated by the addition of the toluene solution in which the catalyst was dissolved. The polymerization temperature (60 °C in ethylene and 50 °C in propylene copolymerizations) and the partial pressure of ethylene or propylene (1.5 bar) were kept constant during the reaction. After 10 to 60 min, the reaction was stopped, and the polymer was precipitated with a dilute HCl solution in ethanol. The product was isolated by filtering, and washed with ethanol and acetone. Amines were liberated from their hydrochlorides by stirring the copolymers overnight in a 1.0 mol/l NaOH/ethanol solution. Finally the polymers were dried in vacuum at 50 °C.

Polymer characterization

A Waters 150C high-temperature gel permeation chromatograph (GPC) operating at 140 °C and equipped with four Waters Styragel columns (HMW 7, 2*HMW 6E and HMW 2) and a differential refractive index detector was used to determine the molar masses and molar-mass distributions of the polymers. The solvent, 1,2,4-trichlorobenzene, was applied at a flow rate of 1.0 cm^3/min. Columns were calibrated with narrow molar-mass distribution polystyrene standards with use of a universal calibration method. A linear low-density polyethylene and polypropylenes with known molar-mass values were used as references in the selection of Mark-Houwink parameters, K and α, for the samples.

The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 300-MHz NMR spectrometer at 125 °C from samples dissolved in 1,1,2,2-tetrachloroethane-d_2 (2 wt % for ^1H and 5 wt % for ^{13}C measurements). The ^1H NMR spectra were recorded with a 5-mm probe, a 60° pulse angle and a pulse repetition time of 8 s, and 1500–3000 transients were accumulated. In the ^{13}C NMR measurements, 4000–8000 transients were accumulated using a 10-mm probe, continuous proton decoupling, a 60° pulse angle and a pulse repetition time of 8 s. The solvent resonances (δ_H 5.91 ppm and δ_C 74.4 ppm) were used as internal references in the NMR spectra. The comonomer contents were calculated from ^1H NMR spectra using the triplet (singlet in amine **13**) arising from protons attached to the methylene carbon next to amide carbonyl (δ_H. 2.0–2.2 ppm) or amine group (δH 2.8–2.9 ppm).

Melting temperatures (T_m) of the polymers were determined with a Mettler Toledo DSC 821^e differential scanning calorimeter. The melting endotherms were measured during the reheating of the polymer sample to 160 °C at a heating rate of 10 °C/min.

Results and discussion

Copolymerizations of amides with ethylene and propylene

Five differently substituted amides of 10-undecenoic acid (**1**-**5**) were synthesised and used in copolymerizations with ethylene and propylene. The results of the copolymerizations (Table 1) show that the activity of the catalyst decreased drastically relative to the homopolymerization of ethylene and propylene in copolymerizations of the amides even though concentrations of the comonomer were low and Al/comonomer molar ratios high. The lower rate of polymerization is likely due to the formation of a stable complex between the active catalyst and the free electron pairs of the amide group. The comonomers **1** and **2** seemed to be slightly less poisonous to the catalyst than were comonomers **3**-**5**. A possible explanation for this is that comonomers with an acidic hydrogen are capable of reacting with MAO (or with the trimethylaluminium which it contains), which reduces their reactivity towards the active catalyst. No significant differences were observed among dimethyl-, diethyl-, and diisopropyl-substituted amides in either reactivity or the activity of the catalyst.

Table 1. Data of copolymerizations of amides **1-5** with ethylene and propylene[a]

Run	Monomers	$c_{com.}$ mmol/ dm^3	Al/Com. mol/ mol	A[b]	Com. in Polymer mol %	M_w kg/ mol	M_w/M_n	T_m °C
E1	Ethylene	-	-	14 400	-	188	3.2	137
E2	Et/1	1.7	40.0	3 800	0.24	107	3.2	130
E3	Et/1	3.3	20.0	330	0.57	53	3.3	127
E4	Et/2	1.3	50.0	2 900	0.33	69	2.7	133
E5	Et/3	1.7	40.0	< 30	n.d.[c]	n.d.	n.d.	n.d.
E6	Et/4	1.7	40.0	190	0.43	18	3.0	127
E7	Et/4	5.0	26.7	40	1.3	5.7	2.5	124
E8	Et/5	1.7	40.0	130	0.58	10	2.4	126
P1	Propylene	-	-	5 800	-	68	2.1	148
P2	Pr/1	1.7	80.0	1 500	0.04	43	2.1	146
P3	Pr/1	2.5	40.0	650	0.14	41	2.1	146
P4	Pr/1	3.3	26.7	80	0.71	23	2.3	139
P5	Pr/2	1.7	80.0	460	0.24	26	2.2	144
P6	Pr/2	2.5	40.0	190	0.48	21	2.0	143
P7	Pr/3	1.7	80.0	200	0.40	31	2.2	142
P8	Pr/3	2.5	40.0	140	0.27	26	2.1	143
P9	Pr/4	1.7	80.0	870	0.14	35	2.1	145
P10	Pr/4	2.5	40.0	250	0.62	22	2.0	141
P11	Pr/5	1.7	80.0	230	0.45	22	2.1	142
P12	Pr/5	2.5	40.0	30	0.96	13	1.9	136

[a] Polymerization conditions, for ethylene polymerizations: catalyst $Et(Ind)_2ZrCl_2/MAO$, [Zr] = $1.7 \cdot 10^{-5}$ mol/dm^3 (run E1 [Zr] = $3.3 \cdot 10^{-6}$ mol/dm^3 and run E7 [Zr] = $6.7 \cdot 10^{-5}$ mol/dm^3), Al/Zr = 4000 mol/mol (run E7 2000 mol/mol), T_p = 60°C, $p_{ethylene}$ = 1.5 bar; for propylene polymerizations: catalyst $Me_2Si(2\text{-}MeInd)_2ZrCl_2/MAO$, [Zr] = $6.7 \cdot 10^{-5}$ mol/dm^3 (run P1 [Zr] = $1.7 \cdot 10^{-5}$ mol/dm^3), Al/Zr = 2000 mol/mol, T_p = 50°C, $p_{propylene}$ = 1.5 bar; [b] Activity of the catalyst in kg of polymer/ (mol Zr ·h); [c] Not determined

Despite their impairment of catalyst activity, all amide comonomers **1-5** formed copolymers with ethylene and propylene. The conversion of the comonomer ranged from 22 to 68% in ethylene copolymerizations and from 12 to 57% in propylene copolymerizations. The decrease in melting temperatures of the copolymers with increasing comonomer content is an indication of random-like incorporation of the comonomer. The ^{13}C NMR spectra established the formation of copolymers with isolated amide-functional branches. Resonances characteristic of aliphatic carbons of the comonomer branch and polymer end groups can be identified in the spectra of the copolymers from runs E7 and P12 (Figures 2 and 3).

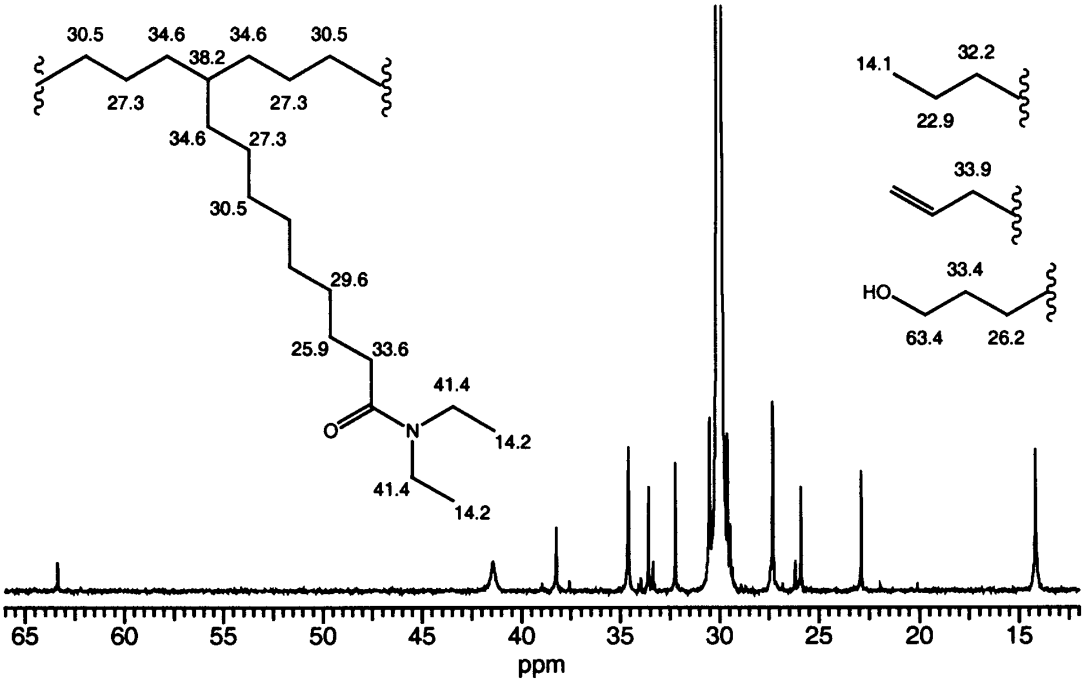


Figure 2. ^{13}C NMR spectrum of poly(ethylene-*co*-**4**), run E7

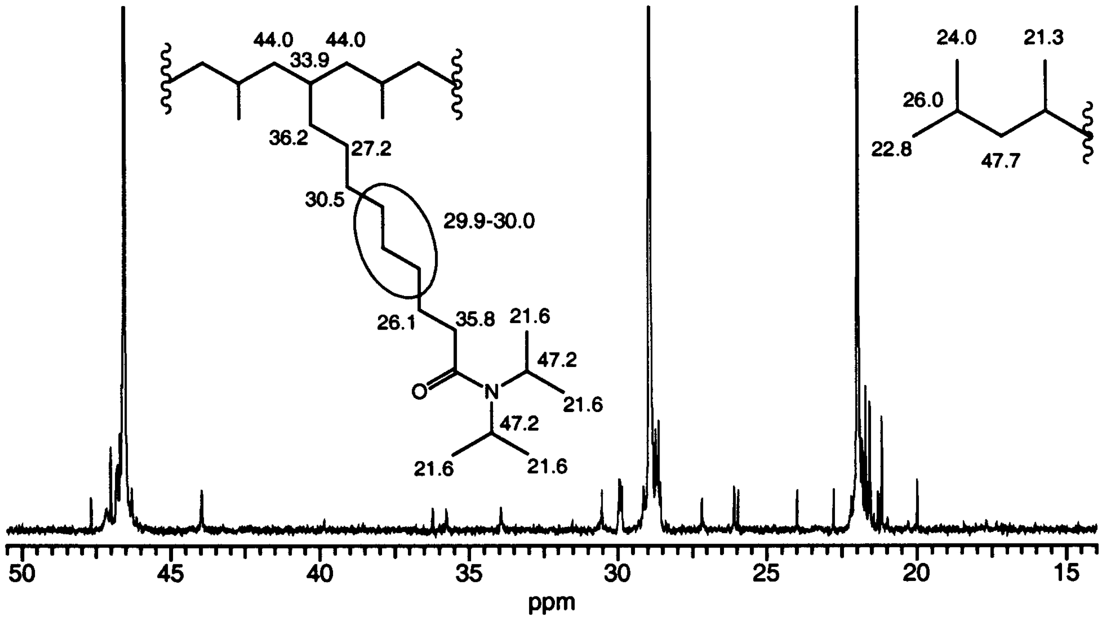


Figure 3. ^{13}C NMR spectrum of poly(propylene-*co*-**5**), run P12

The molar masses of the copolymers were much lower than the molar masses of the homopolymers. According to ^{13}C NMR study, the predominant end groups were saturated linear and isobutyl chain ends in the ethylene and propylene copolymers, respectively. This is a clear indication of chain transfer to cocatalyst MAO, which is known to occur with zirconocene catalysts if the productivity is low and aluminium concentrations are high [22]. It seems that the presence of bulky, Al-complexed comonomer in the polymerization favours the chain transfer to aluminium. The Al-terminated chain ends are usually converted to saturated groups by hydrolysis with acidic alcohol solution. In some ethylene copolymers, e.g. run E7, also a small amount of long-chain primary alcohol groups was visible in the ^{13}C NMR spectra (Figure 2). Evidently, these were formed by oxidation of the Al-terminated polymer chains when the copolymer solution was exposed to air for a short period before the ethanol solution was added. In fact, a similar procedure has been presented as a possible route to end-functionalized polyolefins [23].

Copolymerizations of amines with ethylene

To further study the possibility of preparing nitrogen-functionalized polar olefin copolymers, a number of primary, secondary and tertiary amines were synthesised and used as comonomers in copolymerizations with ethylene. The results are summarized in Table 2. Judging by the values of polymerization activity, amine comonomers as a whole are much better tolerated by metallocene catalyst than are the corresponding amide comonomers. The higher comonomer concentrations could be used without increasing the concentrations of catalyst or cocatalyst, and moderate ethylene polymerization rates were still achieved.

Table 2. Data of copolymerizations of amines **6-13** with ethylene[a]

Run	Comonomer	$c_{com.}$ mmol/ dm^3	Al/Com. mol/ mol	A[b]	Com. in Polymer mol %	M_w kg/ mol	M_w/M_n	T_m °C
E1	-	-	-	14 400	-	188	3.2	137
E9	**9**	16.7	4.0	950	0.92	13	2.1	122
E10	**13**	6.7	10.0	2200	0.28	26	2.4	128
E11	**6**	16.7	4.0	1700	0.84	14	1.6	124
E12	**6**	33.3	4.0	1500	1.2	11	1.7	120
E13	**7**	16.7	4.0	1400	0.65	16	2.3	124
E14	**12**	6.7	10.0	3000	0.37	23	1.7	127
E15	**12**	16.7	4.0	2100	0.92	17	2.2	121
E16	**8**	6.7	10.0	1900	0.40	22	2.3	127
E17	**8**	16.7	4.0	1400	0.70	12	2.0	125
E18	**11**	6.7	10.0	2200	0.32	65	3.8	127
E19	**11**	16.7	4.0	1500	0.60	21	2.3	124
E20	**10**	6.7	10.0	2700	0.28	28	2.0	127
E21	**10**	16.7	4.0	2500	0.49	23	2.1	124

[a] Polymerization conditions, catalyst $Et(Ind)_2ZrCl_2$/MAO, [Zr] = $1.7 \cdot 10^{-5}$ mol/dm^3 (run E1 [Zr] = $3.3 \cdot 10^{-6}$ mol/dm^3), Al/Zr = 4000 mol/mol (run E12 8000 mol/mol), T_p = 60°C, $p_{ethylene}$ = 1.5 bar; [b] Activity of the catalyst in kg of polymer/ (mol Zr ·h)

The reactivity of the comonomer, determined by the incorporated functionality in the copolymer, was decreased when the bulkiness of the ligands around the nitrogen atom was increased. At the same time the productivity of the catalyst was slightly increased. A plausible explanation for this is that the steric hindrance due to the larger groups joined to nitrogen prevents the free electron pairs from forming complexes with the active catalyst. The conversion of amine comonomers varied between 10 and 48%.

As with the amide comonomers, the molar masses of the amine-functionalized polyethylenes were distinctively lower than the molar mass of ethylene homopolymer prepared under the same polymerization conditions. Again, the ^{1}H and ^{13}C NMR spectra showed a high concentration of saturated chain ends and almost complete absence of double-bond resonances, which indicates the importance of chain transfer to aluminium as chain termination mechanism. The type of amine group, i.e. primary, secondary or tertiary, did not affect the molar mass of the copolymer. The NMR measurements demonstrated that the amine functionality was unaltered in the copolymer [24] and there was no indication of adjacent comonomer units. Figure 4 shows the ^{1}H NMR spectra of comonomer **6** and its copolymer with ethylene.

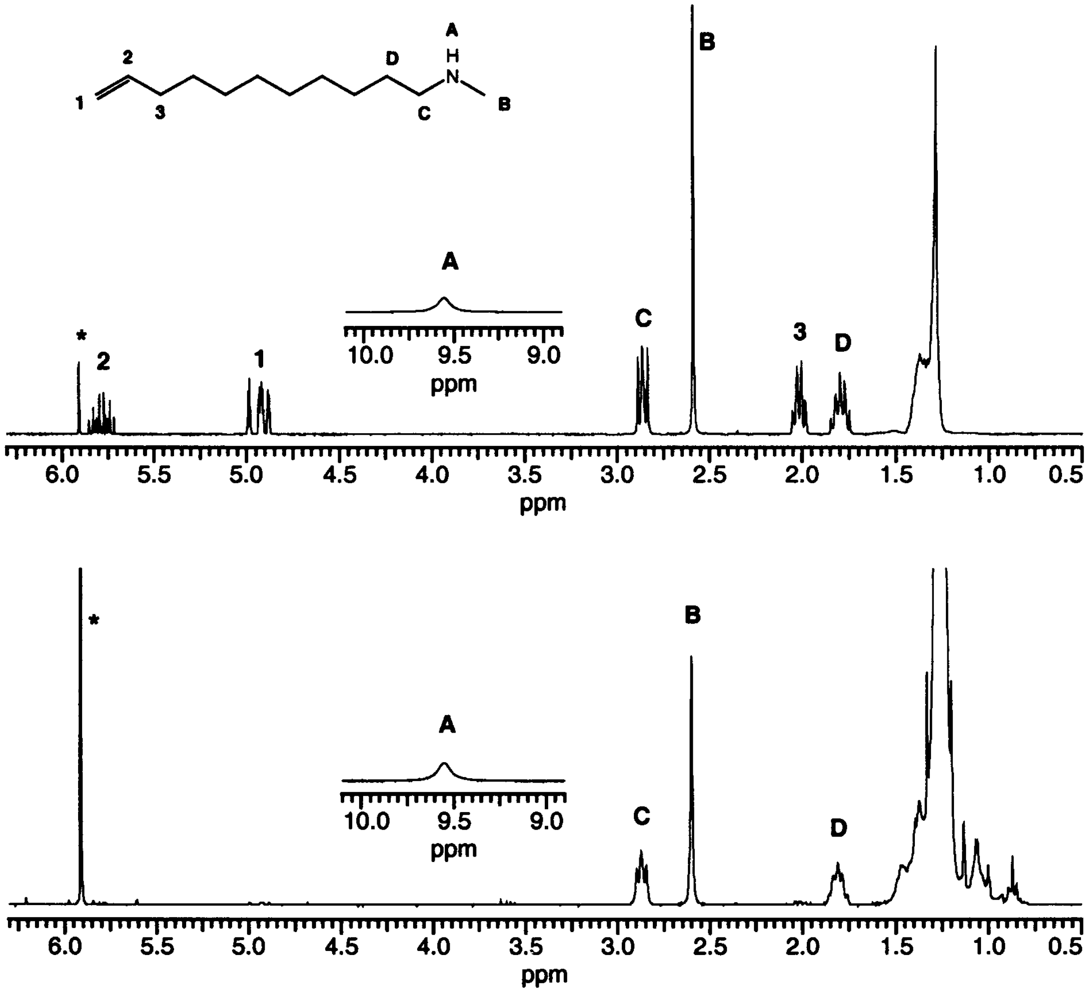


Figure 4. ^{1}H NMR spectra of comonomer **6** (above) and poly(ethylene-*co*-**6**), run E12 (below); the asterisk denotes a solvent resonance

Conclusions

Metallocene/MAO-catalysed copolymerizations of amide- and amine-functional alkenes with ethylene and propylene were successfully performed. The catalyst activity remained higher with the amine functionality. Even the unhindered primary and secondary amines with acidic hydrogens were incorporated in the polyolefin. The use of this kind of comonomer is usually reported to be unsuccessful in transition-metal-catalysed olefin polymerizations [2]. The present results show, however, that the amine-functional comonomers behave in a similar way to the alcohols and ethers that we reported in earlier papers [16].

The copolymerization of nitrogen-functional comonomers with ethylene yielded polymers with structures identical with those of linear low-density polyethylenes except that our products additionally had reactive functional groups in the side chains. Corresponding propylene copolymers with isolated nitrogen-functional branches were synthesised in a similar way. Functionalized copolymers such as these can be utilized, for example, as compatibilizers in polymer blends containing a polyolefin component [25].

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