

# Aminofunctional linear low density polyethylene via metallocene-catalysed ethene copolymerization with N,N-bis(trimethylsilyl)-1-amino-10-undecene

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Ethene was copolymerized with N,N-bis(trimethylsilyl)-1-amino-10-undecene in the presence of homogeneous, MAO-activated *rac*-Me<sub>2</sub>Si(Benz[e]Ind)<sub>2</sub>ZrCl<sub>2</sub> to yield, upon hydrolysis of the silylated amines, short chain branched linear low density polyethylene (LLDPE) with pendent aminoalkyl groups. Aminofunctional LLDPEs were characterized by means of <sup>1</sup>H-n.m.r. FTi.r., elemental analysis and thermal analysis (d.s.c.). Amine functionality, varying between 6 and 19 wt% 1-amino-10-undecene incorporation, influenced significantly the characteristics of LLDPE. Such aminofunctional LLDPEs were applied as reactive intermediates in reactive processing. FTi.r. analysis was applied to monitor the imide-coupling reaction of poly(ethene-co-aminoundecene) with poly(styrene-alt-maleic anhydride). © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Since the pioneering advances of Ziegler and Natta during the early 1950s various families of ethene copolymers with non-polar 1-olefin copolymers have been produced commercially in low pressure processes. The discovery of novel 'single-site' metallocene-based catalysts during the 1980s has greatly facilitated controlled incorporation of non-polar 1-olefins, cycloolefins and styrene into the polyethylene backbone<sup>1</sup>. However, the nature of polyolefin hydrocarbon, reflected by poor adhesion to polar surfaces and interfaces as well as poor dyeability, causes application problems.

Today polar LLDPE is produced either by LLDPE grafting with polar monomers during melt processing or by copolymerizing ethene with polar monomers, e.g. methyl methacrylate, in high pressure free radical processes. In fact, most traditional Ziegler–Natta catalysts are strong Lewis acids which are severely poisoned when traces of polar comonomers (Lewis bases) are added. Therefore, an important objective in low pressure process development is to improve tolerance of polar comonomers<sup>2,3</sup>. One approach to overcome this catalyst poisoning problem is to copolymerize weak olefinic Lewis acids. For instance, Waymouth<sup>4</sup> has developed special MAO-free cationic metallocenes which homo- and copolymerize a variety of sterically hindered polar monomers, e.g. 5-N,N-diisopropylamino-1-pentene or 5-*tert*-butyldimethyl-siloxy-1-pentene. Wilén *et al.*<sup>5</sup>

copolymerized propene with 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol by means of MAO-activated *ansa*-metallocenes. Recently, Löfgren and Aaltonen<sup>6</sup> have used MAO-activated metallocenes to copolymerize ethene with 1-hydroxy-10-undecene, which reacted *in situ* with aluminum alkyls to form aluminates.

In another approach, promoted by Chung *et al.*<sup>7</sup>, borane-functional olefins are copolymerized to form borane-functional olefin copolymers where borane-functional side chains are readily converted into various other functional groups. This synthetic method was applied by Montag<sup>8</sup> who prepared LLDPE with hexylamine side chains via copolymerization of ethene with 9-octenyl-9-borabicyclo[3.3.1]nonane followed by borane conversion.

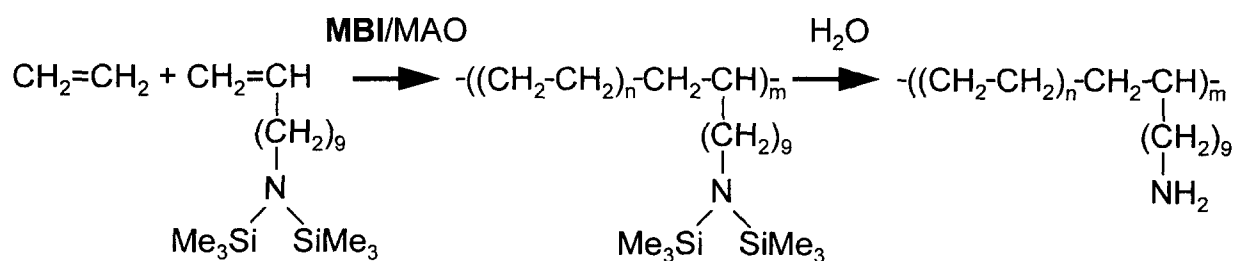
The objective of our research was to incorporate primary alkyl amines as polar short chain branches into polyethylene backbones via metallocene-catalysed ethene copolymerization and to apply such aminofunctional LLDPEs to promote dyeability and coupling reactions with anhydride-functional polymers, e.g. poly(styrene-alt-maleic anhydride).

## EXPERIMENTAL

### Materials

*Rac*-Me<sub>2</sub>Si(2-MeBenz[3]Ind)<sub>2</sub>ZrCl<sub>2</sub> was obtained from BASF AG, 1-octene from Aldrich Co., MAO (10 wt% in toluene, *M*<sub>n</sub> = 1000 g mol<sup>-1</sup>) from Witco, Germany, toluene from Roth GmbH, ethene from

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Scheme 1 Synthesis of aminofunctional LLDPEs

Gerling Holz u. Co., Handels-GmbH, Hamburg. Toluene solvent was rectified over  $\text{LiAlH}_4$  and refluxed and distilled over Na/K alloy prior to use. *Rac*- $\text{Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$ , ethene and MAO were used without further purification. *N,N*-bis(trimethylsilyl)-1-amino-10-undecene was synthesized by the route 10-undecene-1-ol, 1-chloro-10-undecene, 10-undecenyl-1-phthalimide, 1-amino-10-undecene, *N,N*-bis(trimethylsilyl)-1-amino-10-undecene. Metallocenes, MAO, solvent and monomers were handled and stored under dry argon atmosphere.

**Synthesis of 1-chloro-10-undecene.** A three-necked flask, equipped with magnetic stirring and reflux condenser, was charged with 400 ml (340.6 g, 2.0 mol) of 10-undecen-1-ol and pyridine (1 ml). During dropwise addition of 288 ml (476.0 g, 4.0 mol) thionylchloride, ice-cooling was maintained. The reaction mixture was then heated up to  $90^\circ\text{C}$  for about 2 h. The remaining thionylchloride was removed *in vacuo*. The brown product was first washed with saturated aqueous NaCl (400 ml), then with an aqueous solution of  $\text{Na}_2\text{CO}_3$  (10 wt%, 400 ml) and again with 200 ml of saturated aqueous NaCl. The collected aqueous solutions were extracted three times with diethylether. The combined organic layers were dried with  $\text{MgSO}_4$ . Solvent was removed by evaporation at room temperature. The product was distilled using a Vigreux column (boiling point  $58^\circ\text{C}$ ). Yield: 396.6 g (1.96 mol, 98%); purity: 99.5% (g.c.); elemental analysis for  $\text{C}_{11}\text{H}_{21}\text{Cl}$  found (calc.) [wt%]: C, 69.73 (70.00); H, 11.23 (11.22); Cl, 18.43 (18.78);  $^1\text{H-n.m.r.}$  analysis:  $\delta$  [ppm] = 1.35 (m, 12 H,  $\text{CH}_2$ ), 1.78 (m, 2 H,  $\text{ClCH}_2\text{CH}_2$ ), 2.05 (m, 2 H,  $\text{C}=\text{CCH}_2$ ), 3.53 (m, 2 H,  $\text{ClCH}_2$ ), 4.96 (m, 2 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ), 5.80 (m, 1 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ).

**Synthesis of 10-undecenyl-1-phthalimide.** In a three-necked flask, equipped with mechanical stirring and reflux condenser, potassium phthalimide (185.2 g, 1.0 mol) and hexadecyltributylphosphoniumbromide (40.6 g, 0.88 mol) were suspended in toluene (400 ml). After dropwise addition of 1-chloro-10-undecene (151.0 g, 0.8 mol) the mixture was refluxed for 20 h. The mixture was filtered, the inorganic residue washed with ether (200 ml) and the crude product mixture was filtered through neutral  $\text{Al}_2\text{O}_3$ . Elution was continued until thin-layer chromatography (t.l.c.) showed no traces of product. Removal of the solvents *in vacuo* yielded 212.4 g 10-undecenyl-1-phthalimide (0.71 mol, 88.7% melting point:  $42.2^\circ\text{C}$ ). Elemental analysis for  $\text{C}_{19}\text{H}_{25}\text{NO}_2$  found (calc.) [wt%]: C, 76.24 (76.22); H, 8.26 (8.49); N, 4.60 (4.70);  $^1\text{H-n.m.r.}$  analysis:  $\delta$  [ppm] = 1.31 (m, 12 H,  $\text{CH}_2$ ), 1.67 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 2.05 (m, 2 H,  $\text{C}=\text{CCH}_2$ ), 3.67 (m, 2 H,  $\text{NCH}_2$ ), 4.94 (m, 2 H,

$\text{H}_2\text{C}=\text{CHCH}_2$ ), 5.80 (m, 1 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ), 7.70 (m, 2 H, arom.  $\text{CH}$ ), 7.82 (m, 2 H, arom.  $\text{CH}$ ).

**Synthesis of 1-amino-10-undecene (AU).** In a three-necked flask, equipped with mechanical stirring and reflux condenser, 10-undecenyl-1-phthalimide (197.8 g, 0.66 mol) and 50 ml hydrazinehydrate (1.03 mol) were dissolved in 2 l ethylalcohol and refluxed for 5 h. The reaction was monitored by t.l.c. The white precipitate was filtered by suction and washed with diethylether. The combined solvents were removed *in vacuo* and the remaining yellowish solid was taken up in diethylether. Upon standing again, a white precipitate occurred. Filtration, removal of the solvents and distillation yielded 64.2 g (0.38 mol, 57.4%) of a colourless oil (boiling point  $70\text{--}80^\circ\text{C}$ , 1 mbar). Elemental analysis for  $\text{C}_{11}\text{H}_{23}\text{N}$  found (calc.) [wt%]: C, 78.24 (78.03); H, 13.86 (13.69); N, 8.31 (8.27);  $^1\text{H-n.m.r.}$  analysis:  $\delta$  [ppm] = 1.16 (s, 2 H,  $\text{NH}_2$ ), 1.35 (m, 14 H,  $\text{CH}_2$ ), 2.05 (m, 2 H,  $\text{C}=\text{CCH}_2$ ), 2.67 (m, 2 H,  $\text{NCH}_2$ ), 4.96 (m, 2 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ), 5.80 (m, 1 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ).

**Synthesis of *N,N*-bis(trimethylsilyl)-1-amino-10-undecene (BS-AU).** *N*-methyl-*N*-trimethylsilylacetamide (30.12 g, 0.27 mol), 1-amino-10-undecene (22.01 g, 0.13 mol) and 0.5 ml trimethylsilylchloride were stirred at ambient temperature for 1 h. Two layers occurred, the upper one separated and distilled *in vacuo* (Vigreux column, boiling point  $113\text{--}115^\circ\text{C}$ , 1 mbar). Yield: 29.0 g (0.09 mol, 71.2%); purity: 98.25% (g.c.); elemental analysis for  $\text{C}_{17}\text{H}_{39}\text{NSi}_2$  found (calc.) [wt%]: C, 65.11 (65.09); H, 13.15 (12.53); N, 4.47 (4.50);  $^1\text{H-n.m.r.}$  analysis:  $\delta$  [ppm] = 0.05 (s, 18 H, 2  $\text{Si}(\text{CH}_3)_3$ ), 1.35 (m, 14 H,  $\text{CH}_2$ ), 2.05 (m, 2 H,  $\text{C}=\text{CCH}_2$ ), 2.67 (m, 2 H,  $\text{NCH}_2$ ), 4.96 (m, 2 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ), 5.80 (m, 1 H,  $\text{H}_2\text{C}=\text{CHCH}_2$ ).

#### Polymerization

Polymerization reactions were performed in a glass reactor rinsed, prior to use, with 150 ml of a  $0.03\text{ mol l}^{-1}$   $\text{AliBu}_3$  solution in toluene. Typically, 85 ml toluene, 2.8 ml BS-AU and 10 ml MAO were pumped into the glass reactor. The total volume of the reaction mixture was 100 ml at all polymerizations. After thermal equilibration of the reactor system, ethene was continuously added by a mass-flow meter (F-111C, Bronkhorst, NL-7261 AK Ruurlo, The Netherlands) until the reaction mixture was saturated with ethene (2.0 bar). The polymerization was started by adding  $1.0\ \mu\text{mol}$  of *rac*- $\text{Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$  in 2 ml toluene, equivalent to  $[\text{Zr}] = 10\ \mu\text{mol l}^{-1}$  and  $[\text{Al}] = 160\ \text{mmol l}^{-1}$ . During polymerization, the pressure of ethene was kept constant. The polymerization was quenched with 5 ml methanol after 10 min. To the quenched reaction mixture

200 ml methanol was added to precipitate the polymer. During magnetic stirring an aqueous solution of HCl ( $10 \text{ mol l}^{-1}$ ) was added 1 ml-wise, until the pH of the mixture remained constant at  $\text{pH} = 2$ . Stirring was continued for 10 h. After the addition of 300 ml of an aqueous solution of HCl ( $\text{pH} = 2$ ) the polymer was separated by filtration, washed twice with 100 ml of an aqueous solution of HCl ( $\text{pH} = 2$ ), then twice with 200 ml distilled water, twice with 100 ml of a fresh prepared aqueous solution of NaOH ( $\text{pH} = 13$ ) and thrice with 200 ml distilled water. The polymer was then dried at  $70^\circ\text{C}$  *in vacuo*.  $^1\text{H}$ -n.m.r. analysis showed  $\text{CH}_2\text{N}$  signals at  $\delta = 2.67$  ppm and no monomer signals ( $\text{CH}_2=\text{CH}-\text{R}$ ) at  $\delta = 4.96$  ppm and 5.80 ppm.

### Characterization

All  $^1\text{H}$ -n.m.r. spectra were recorded with a Bruker ARX 300. For monomer characterization,  $\text{CDCl}_3$  was used as solvent at 300 K. Polymer characterization was performed in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 400 K.

For d.s.c. analysis a Perkin-Elmer 'Series 7' apparatus was used. Temperature programme: (1)  $30^\circ\text{C} \rightarrow 150^\circ\text{C}$ , heating rate  $10 \text{ K min}^{-1}$ ; (2)  $150^\circ\text{C}$ , held for 10 min; (3)  $150^\circ\text{C} \rightarrow 30^\circ\text{C}$ , cooling rate  $5 \text{ K min}^{-1}$ ; (4)  $30^\circ\text{C} \rightarrow 150^\circ\text{C}$ , heating rate  $10 \text{ K min}^{-1}$ . The second heating rate was used for determination of melting points ( $T_m$ ).

The bilayer sample for FT-i.r. analysis was prepared by the following procedure. The poly(styrene-alt-maleic anhydride) component was dissolved in  $\text{CHCl}_3$  and casted on a KBr plate. The complementary AU-E component was hot-melt pressed to a total film thickness of about  $3 \mu\text{m}$ . Both were put together in a bilayer and heated to  $230^\circ\text{C}$ . The FT-i.r. spectra were recorded with a Bruker IFS 88 spectrometer. For signal averaging, 100 scans were taken and a liquid nitrogen-cooled MCT detector was used.

**Table 1** Poly(ethene-co-aminoundecene)

Run No.	MJS109	MJS110	MJS111
[Ethene] feed ( $\text{mol l}^{-1}$ ) <sup>a</sup>	0.210	0.210	0.210
[Ethene] feed (mol%)	75	85	92
[BS-AU] feed ( $\text{mol l}^{-1}$ )	0.072	0.036	0.018
[BS-AU] feed (mol%)	25	15	8
MBI concentration ( $\mu\text{mol l}^{-1}$ )	10	10	5
[Al] <sup>b</sup> ( $\text{mol l}^{-1}$ )	160	160	160
Catalytic activity <sup>c</sup>	380.000	1.280.000	2.980.000
N content <sup>d</sup> (wt.%)	1.56	1.05	0.48
AU <sup>e</sup> (mol%)	3.70	2.35	1.01
AU <sup>e</sup> (wt.%)	18.8	12.7	5.8
$T_m^f$ ( $^\circ\text{C}$ )	100.9	109.0	115.6
$\Delta H_m^f$ ( $\text{J g}^{-1}$ )	55.6	68.3	74.9

<sup>a</sup> Ethene pressure: 2 bar

<sup>b</sup> [Al] relating to MAO content

<sup>c</sup> Calculated as inserted monomer units (mol) divided by monomer concentration ( $\text{mol l}^{-1}$ ), amount of catalyst (mol) and time (h)

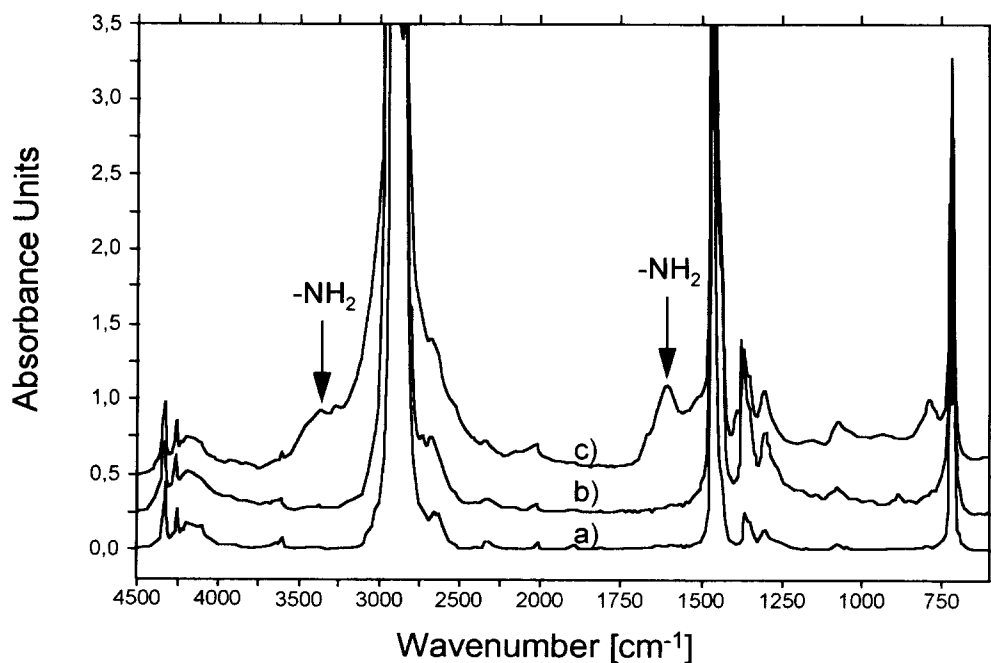
<sup>d</sup> Determined by elemental analysis

<sup>e</sup> Of the copolymer

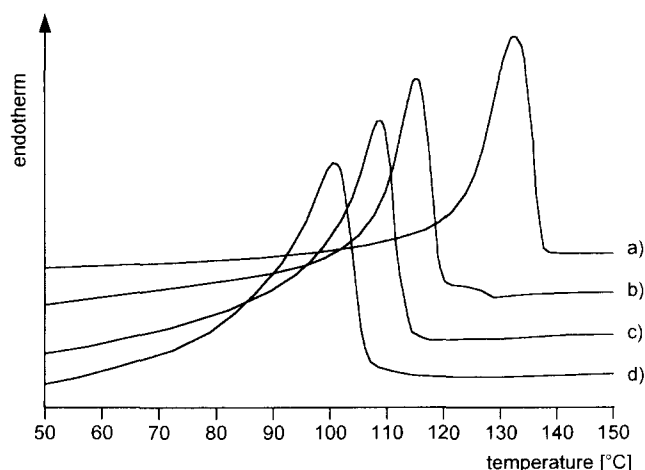
<sup>f</sup> Determined by d.s.c. measurements at a constant heating rate of  $10 \text{ K min}^{-1}$ ; data of second heating

## RESULTS AND DISCUSSION

Bissilylation of amine-functional 1-olefins was applied successfully to overcome catalyst poisoning resulting from either complexation of amine-containing Lewis bases or cleavage of transition metal carbon bonds by acidic hydrogen of the amine groups. In comparison to amines, the corresponding bissilylated amines are much weaker Lewis bases and are tolerated by metallocene catalysts. N,N-bis(trimethylsilyl)-1-amine-10-undecene, abbreviated as BS-AU, prepared by bissilylating 1-amino-10-undecene, abbreviated as AU, was copolymerized with ethene in toluene solvent in the presence of MAO-activated  $\text{rac-Me}_2\text{Si}(\text{Benz}[e]\text{Ind})_2\text{ZrCl}_2$  at  $40^\circ\text{C}$  using an [Al]/[Zr] molar ratio of 16 000 (cf. Scheme 1). Hydrolysis of the silylated amines was achieved either by steaming or by treating the copolymer with aqueous



**Figure 1** FTi.r. spectra of polyethene (a), poly(ethene-co-1-octene) with 12.0 mol% 1-octene (b), and poly(ethene-co-aminoundecene) containing 19 wt% AU (c)

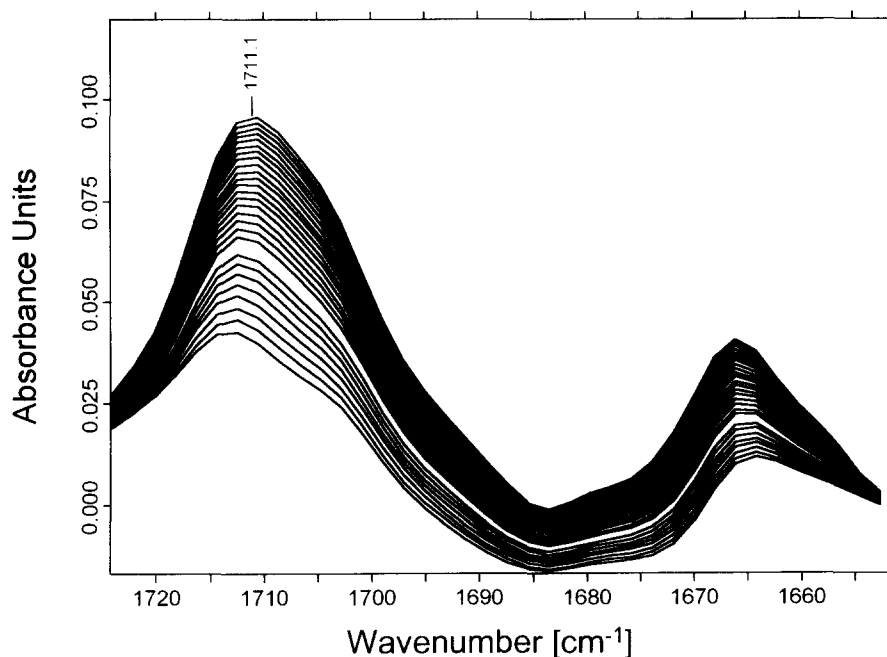


**Figure 2** D.s.c. traces of poly(ethylene (a) and poly(ethylene-*co*-aminoundecene) containing 6 wt% (b), 13 wt% (c) and 19 wt% (d) AU

from 6 to 19 wt% reduced the melting temperature from 116 to 101°C and lowered  $\Delta H_m$  from 75 to 56 J g<sup>-1</sup>. Typical d.s.c. traces are displayed in *Figure 2*.

Interestingly, even at low AU incorporation, the resulting poly(ethylene-*co*-aminoundecene) was insoluble in traditional solvents used to dissolve LLDPE although residual aluminium, which is an amine complexing agent, was carefully removed and the samples were handled under argon to prevent carbonate formation with carbon dioxide. Similar solution behaviour was reported by Montag<sup>8</sup> who prepared aminohexyl-functional ethene copolymers via the borane route. In consequence, it was not possible to perform viscosity measurements or size exclusion chromatography to determine molecular masses. However, the resulting copolymers were mouldable and films and mouldings were obtained.

Amine groups of aminofunctional LLDPE can be converted into a great variety of other functional groups.



**Figure 3** Accumulated FTi.r. spectra of poly(styrene-*co*-maleic anhydride)/poly(ethylene-*co*-aminoundecene) films which form an imide-coupled interlayer at 230°C. Spectra were recorded at 3 min intervals

HCl, followed by aqueous NaOH. The polymerization conditions and copolymer properties are listed in *Table 1*.

The BS-AU content in the monomer feed was varied from 8 to 25 mol%, corresponding to [Al]/[BS-AU] molar ratios varying from 2 to 9. According to elemental analysis, and confirmed by <sup>1</sup>H-n.m.r. studies, AU incorporation varied from 1 to 3.7 mol% which is equivalent to 6 to 19 wt%. The presence of amine groups was detected by means of FTi.r. analysis. FTi.r. spectra are displayed in *Figure 1*. With increasing BS-AU content in the comonomer feed, catalyst activity decreased markedly. This activity decay is similar to that observed when the less reactive, non-functionalized 1-undecene is copolymerized with ethene.

Similarly to ethene copolymerization with non-polar 1-olefins, AU incorporation affords short-chain branching which reduces both melting temperatures and crystallinity, which is reflected by the heat of fusion  $\Delta H_m$  reported in *Table 1*. Increasing the AU content

For example, isocyanates react with amines in melt or decalin solution to form ureas. This will be reported elsewhere in more detail. Another important analogous polymer reaction is the reaction of aminofunctional LLDPE with anhydride-functional polymers which are readily available either by maleic anhydride copolymerization or maleic anhydride grafting. The formation of imides resulting from the coupling reaction of poly(styrene-*co*-maleic anhydride) with poly(ethylene-*co*-aminoundecene) was monitored by means of FTi.r. spectroscopy. To study the imide-coupling reaction occurring at interfaces, a film of poly(ethylene-*co*-aminoundecene), containing 19 wt% AU, was sandwiched with a film of poly(styrene-*co*-maleic anhydride) containing 16 wt% maleic anhydride. At 230°C i.r. absorption at 1711 cm<sup>-1</sup> is typical for imide groups. This is shown in *Figure 3* in which imide formation is monitored at 230°C during a period of 15 to 90 min with FTi.r. spectra recorded at intervals of 3 min. This clearly

demonstrates the formation of covalent bonds between the two incompatible polymers, thus improving interfacial adhesion and compatibility.

In conclusion, bissilylation of aminofunctional 1-olefins and copolymerization in the presence of metallocene catalysts represents an attractive synthetic route to novel families of functionalized ethene copolymers.

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