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Studies on metallocene catalyzed copolymers of ethylene with 10- undecen- 1- ol

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Ethylene was copolymerized with 10-undecen-1- ol in the presence of four different metallocene catalyst systems. The copolymers were characterized by differential scanning calorimeter (DSC) and by dynamic mechanical analysis (DMA). It was demonstrated that properties of the catalysts used affected the crystallization behaviour of the copolymers because the catalysts exhibited differences in conversions of the polar comonomer. The step crystallization technique using DSC provided useful information about the differences in comonomer incorporation in the chain. The formation of multiple peaks, based on differences in ethylene sequence length, is much weaker for the copolymers produced with a non- bridged metallocene, than for polymers produced with bridged catalysts. A study of the crystallization rates in nonisothermal experiments exhibited a small decrease in crystallization temperatures with increasing branching. The Hoffman-Weeks extrapolation of melting point vs crystallization temperature gave reasonable results for silylene-bridged copolymers. In DMA, study was made of the storage modulus as an indicator of stiffness and loss tangent as a measure of the effect of branching on the β-relaxations. The DMA measurements indicated a slight increase in the flexural modulus, or stiffness values, of the copolymers relative to the corresponding homopolymers. The damping curves did not show any peaks in the β-relaxation range, which indicates that the amount of short branching in the copolymers is negligible. *© 2000 Kluwer Academic Publishers*

1. Introduction

The incorporation of bulky and functional groups into polyolefins has been an area of long standing interest in our research group, as it represents a useful method for modifying the chemical and physical properties of polyolefins [1–6]. Polyolefins containing functional groups in the right composition show improved adhesive, thermal, morphological and mechanical properties, improved affinity for dyes and printing agents, and in addition they are more compatible with other polymers [7].

Our investigations have shown, that several metallocene catalysts promote the copolymerization of ethylene and propylene with comonomers that contain hydroxyl, acid and ester groups [8]. The capabilities of the catalysts to polymerize polar comonomers were different and depended strongly on the catalyst structure [2]. However, information about the length of the ethylene sequences in such copolymers studied has been missing, as also knowledge of how the melting points are affected by the comonomer content and the crystallization rates.

Recently segregation studies by stepwise annealing using differential scanning calorimeter (DSC) have been applied on different types of metallocene catalyzed ethylene-copolymers [9–18]. The results have shown that differences in the ethylene sequence distributions can be seen when the polymers are annealed in steps at successively lower temperatures. The multiple endothermic peaks observed in the melting curves after this heating treatment correspond to a fraction of segregated molecules which crystallized at a certain temperature. These multiple peaks also indicate several distinct lamellar thickness populations. Reports of these techniques for the characterization of functionalized polyolefins have been missing, but recently a method inducing molecular segregation during crystallization [19] has been applied on the characterization on grafted maleic anhydride ultra low density polyethylene.

In order to better understand the incorporation of the polar comonomers in the chain, functionalized copolymers of ethylene and 10-undecen-1-ol, synthesised with various zirconocene catalysts together with methylaluminiumoxane (MAO), were analyzed by DSC. As dynamic mechanical analysis (DMA) has proved [20–24] to be sensitive to the structural heterogeneity of polyethylene and ethylene copolymers this technique was also applied in our investigations on some of the ethylene-alcohol copolymers in order to get a more complete picture of the comonomer incorporation and an idea of the mechanical properties of the polymers. This is of major interest for us, because the small amounts of polymer, obtained from lab-scale polymerizations, do not allow any large scale mechanical testing.

2. Experimental

2.1. Chemicals

The catalysts *rac*-dimethylsilylbis(1-indenyl) zirconium dichloride $Me_2Si(Ind)_2ZrCl_2$ (Cat 1), and *rac*-dimethylsilylbis (2-methyl-l-indenyl)zirconium dichloride $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ (Cat 4) were synthesised according to Spaleck *et al.* [25]. *Rac*-ethylenebis (1-indenyl)zirconium dichloride $Et(Ind)_2ZrCl_2$ (Cat 2), bis(1-indenyl)zirconium dichloride $(Ind)_2ZrCl_2$ (Cat 3), and cocatalyst methylaluminoxane (MAO, a 10 wt% solution in toluene) were purchased from Witco GmbbH and used as received. The comonomer 10-undecen-1-ol was obtained from Fluka and was purified with molecular sieves (0.3 nm). The structures of the catalysts used are shown in Fig. 1.

2.2. Copolymerizations

The copolymerizations were conducted in a 0.25 dm^3 glass autoclave at 25 °C and 2.0 bar monomer gas pressure. The method of polymerization has been described in detail in a previous report [2].

2.3. Polymer characterization

The formation of a true ethylene copolymer with 10-undecen-1-ol was characterized by ^{13}C NMR spectroscopy as reported earlier [2]. Comonomer contents were calculated from ^1H NMR spectra recorded on a Varain 2000 300 MHz spectrometer at 125 °C from samples dissolved in 1, 1, 2, 2-tetrachlorethane-d_2. Molar masses (MW) and molar mass distributions (MMD = D in Table I) were determined with a Waters 150C gel permeation chromatograph (GPC) operating at 140 °C using 1, 2, 4-trichlorbenzene as eluent. The characteristics of the samples are given in Table I.

All melting and crystallization studies were made with a Perkin - Elmer DSC 7 differential scanning calorimeter. The temperature calibration was made with Indium (m.p. 156.6 °C) and for the temperature/area calibration the heat capacity value 28.46 J/g was used. In order to study the influence of the hydrogen bonds on the crystallization behaviour a study of the crystallization rates was performed. The powder samples (2–3 mg) were first heated to 160 °C and then cooled at different cooling rates (5, 10, 20 and 30 °C/min) down to 10 °C. The samples were kept at this temperature for 2 minutes and then corresponding melting endotherms were run at a heating rate of 10 °C/min. The melting points given in Table I are those obtained after the crystallization cycle of 10 °C/min and the crystallinities of the polymers were determined from the same curves by taking the value 290 J/g for the enthalpy of fusion of perfectly crystalline polyethylene.

The step crystallizations by annealing at successively lower temperatures were carried out using the DSC-7 according to a procedure described earlier [12, 14]. The temperature stages were separated from each other by 6 °C with a holding time of 120 minutes at each annealing temperature. In this investigation the functionalized copolymers were all annealed with the program SFT140, that is, the annealing covered

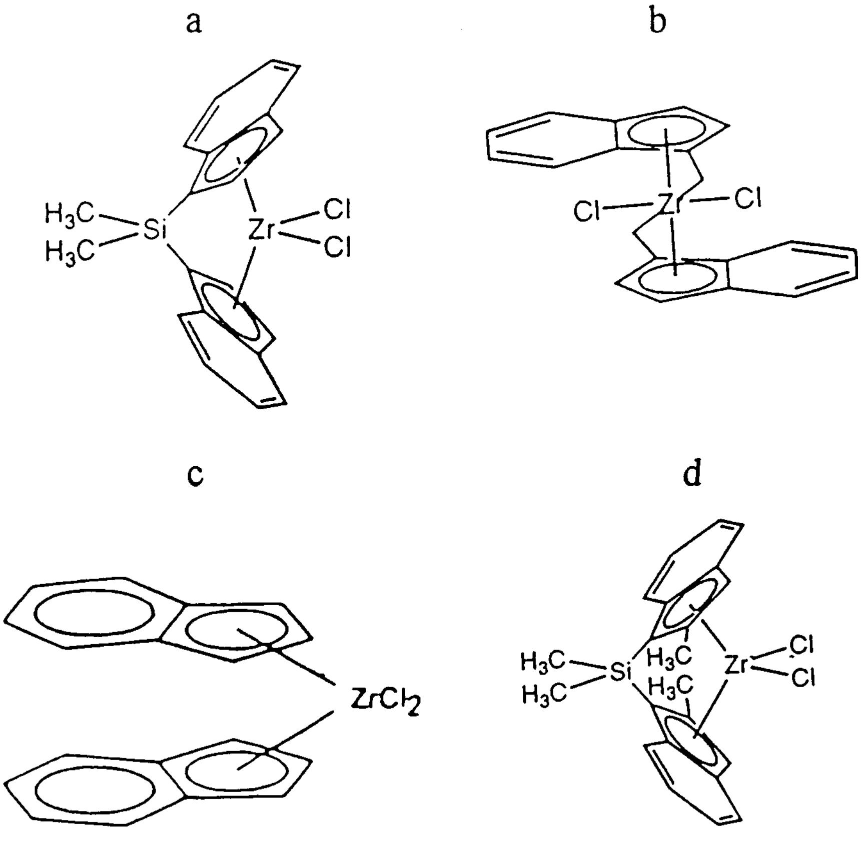


Figure 1 Structures of catalyst used in the polymerizations: a) $Me_2Si(Ind)_2ZrCl_2$ (Cat 1), b) $Et(Ind)_2ZrCl_2$ (Cat 2), c) $(Ind)_2ZrCl_2$ (Cat 3), and d) $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ (Cat 4).

TABLE I Properties of ethylene -10-undecen-1-ol copolymers produced with different catalyst systems: Cat 1 = $Me_2Si(Ind)_2ZrCl_2$/MAO (Series 100), Cat 2 = $Et(Ind)_2ZrCl_2$/MAO (Series 200), Cat 3 = $(Ind)_2ZrCl_2$/MAO (Series 300), and Cat 4 = $Me_2Si(2\text{-}MeInd)_2ZrCl_2$/MAO (Series 400)

polymer	catalyst	alcohol in feed (moldm^{-2}) ×10^2	alcohol found in polymer wt%/mole%	MW (g/mol) × 10^{-3}	D	E′(25°C) (Pa)	M.p (°C)	X$_c$ (%)
100-15	$Me_2Si(Ind)_2ZrCl_2$	0	—	467	2.6	1.12×10^9	124.1	45.3
100-18	”	0.3	0.36/0.06	488	2.9	1.65×10^9	127.9	45.7
100-19	”	0.6	0.53/0.09	324	2.5	1.49×10^9	128.6	41.5
100-20	”	0.9	n.a	215	2.3	1.43×10^9	123.9	40.5
100-22	”	1.6	7.1/1.3	155	2.4	n.a.	119.3	33.0
201-07	$Et(Ind)_2ZrCl_2$	0	—	353	3.2	n.a	124.0	45.1
201-10	”	0.9	3.2/0.52	184	2.4	n.a	128.0	46.3
201-14	”	2.2	5.4/0.88	124	2.3	n.a.	130.1	47.8
301-01	$(Ind)_2ZrCl_2$	0	—	673	2.4	1.19×10^9	134.8	50.0
301-02	”	0.9	0.85/0.14	573	2.2	1.19×10^9	128.5	40.0
301-08*	”	2.2	1.9/0.31	127	2.9	1.30×10^9	128.4	54.8
401-01	$Me_2Si(MeInd)_2ZrCl_2$	0	—	575	2.6	1.43×10^9	132.3	49.3
401-02	”	0.6	n.a	407	2.4	1.50×10^9	125.4	45.0
401-03	”	1.2	0.69/0.11	303	2.3	1.37×10^9	120.0	36.0
401-04	”	1.9	8.0/1.4	203	2.2	n.a.	121.6	35.9.

*The copolymerization was conducted at 70 °C

the temperature range from 140 °C to 92 °C and annealing was performed at 140 °C, 134 °C, 128 °C, 122 °C, 116 °C, 110 °C, 104 °C, 98 °C and 92 °C respectively. This choice of just one range made it easier to compare the comonomer incorporation for different samples. In order to get comparisons of the heterogeneities between different copolymers a distribution index, DI, was used [14, 26]. The height of the “linear” peak in the endotherm obtained after the annealing procedure was given the value 1 and was compared to the height of the separated peaks. Smaller “secondary” peaks gave lower DI-numbers. This concept was used for some comparisons of the heterogeneity of the distributions.

For the DMA measurements proper specimens of the functionalized copolymers were obtained by applying an alternative procedure to the earlier used method [23]. The specimens were prepared in a co-rotating twin-screw midiextruder (DSM, capacity = 16×10^{-6} m^3, screw length $L = 150$ mm) under nitrogen atmosphere connected to a mini-injection moulder (DSM).

The experimental conditions were as follows: homogenization time in the extruder 5 min, temperature of the extruder 220 °C, rotational speed 65 rpm. Smooth plaques of the dimensions 1.5 mm × 4 mm × 18 mm were then obtained.

The DMA measurements were performed with the Perkin Elmer DMA 7 instrument equipped with Unix software and three point bending geometry. The analyses were run in the temperature scan mode from −135 °C to about 110 °C. The frequency was 1 Hz and the heating rate 4 °C/min. The storage modulus (E'), the loss modulus (E'') and tan δ were calculated from the experimental runs.

3. Results and discussion

3.1. DSC measurements

The behaviour of the different metallocenes in present polymerizations affected the melting points (m.p) and crystallinity data given in Table I. The catalyst Me_2Si $(Ind)_2$ $ZrCl_2$ (Cat1) as well as the catalyst Et $(Ind)_2$ $ZrCl_2$ (Cat2) are known to possess in ethylene polymerizations the ability to form vinyl ended macromonomers and to insert the macromonomers and therefore causing long chain branching (LCB) [27]. LCB formation occurs especially at low ethylene concentrations, which is the case in the ethylene homopolymerizations with Cat1 and Cat2 (run 100- 15 and run 201- 07 in Table I) [2], which explains the low melting points as well as the low crystallinity of these homopolymers. The addition of the polar comonomer decreases the ethylene polymerization rate quite dramatically on that the ethylene concentration is high through the whole copolymerization process, giving first copolymers with somewhat higher melting temperatures and crystallinities, but when a bigger amount of the polar comonomer is incorporated the melting temperatures decrease. The non- bridged catalyst $(Ind)_2ZrCl_2$ (Cat3) is known to be very active in ethylene homopolymerizations, but to have a poor comonomer response and therefore do not insert macromonomers so that a linear ethylene chain with higher melting point and higher crystallinity is obtained (run 301-01 in Table I). According to earlier findings [2], using this catalyst, a broadening of the molar mass distribution takes place with addition of higher amounts of polar monomer. This broadening in the molar mass distribution indicated that the catalyst contains multiple active species which most likely are formed by reactions between functional comonomer and catalyst components. A rather low alcohol amount is incorporated in the copolymer 301-08, and this may lead to a microstructure, which results in a longer sequence of ethylene units to form crystalline phases similar to those in pure high density polyethylene (HDPE) and this may explain the high crystallinity value of polymer 301-08.

The methyl substituted catalyst Me_2 Si $(2\text{-}MeInd)_2$ $ZrCl_2$ (Cat4) was only about half as active as the corresponding nonsubstituted catalysts (Cat1 and Cat2) in homopolymerizations, but on the other hand it displayed the highest conversion of the polar comonomer and furthermore it exhibited somewhat different decay kinetics with addition of comonomer than the other catalysts [2]. With Cat4 the melting points and the crystallinities decreased with increasing comonomer incorporation.

During isothermal crystallization at low supercoolings a crystallization of lamellae with a dimension large enough to be stable at the crystallization temperature will take place but also at higher supercoolings crystallization of smaller crystallites is possible [28]. An isothermal crystallization at decreasing temperatures will thus make it possible to obtain a distribution of lamellarsizer, which can be correlated to the chemical composition distribution (CCD). The lamella thickness has been related to the melting temperature by the Thomson-Gibbs equation

$$T_\mathrm{m} = T_\mathrm{m}^\circ\left(\frac{1-2\delta_e}{\Delta H l_\mathrm{c}}\right) \qquad (1)$$

where T_m is the observed melting point, T_m° is the equilibrium melting point of an infinite polyethylene crystal (414.5 K), l_c is the thickness of the lamellae with melting point T_m, ΔH is the enthalpy of fusion per unit volume (288×10^6 J/m^3, and δ_e is the surface energy of a polyethylene crystal (70×10^{-3} J/m^{-2}) [26]. The Gibbs-Thomson equation has been applied on estimations of the crystal thickness of both very low density ethylene-1-octene-copolymers [29] and high density polyethylenes [30, 31] but also in more deep studies of the correlations between crystal thickness and the surface energies of bundle crystals in low to very low density ethylene-octene metallocene copolymers [32]. According to Lu *et al.* [31] the use of the Thomson-Gibbs equation to calculate the thickness distributions of linear polyethylenes from DSC thermograms is feasible if the value of δ_e is known and the heating rate is restricted to 10 °C/min, but for random copolymers some restrictions imposed by copolymer melting are involved. In this work we applied the Thomson-Gibbs equation for a qualitative comparison of the calculated lamellae thicknesses of the separated peaks from the step crystallization experiments.

The separation into multiple peaks was much weaker in the DSC endotherms obtained after segregation of copolymers containing functionality than in those of ethylene-1-olefin copolymers studied earlier [12, 14, 15, 18]. This was especially true for the functionalized polymers produced with the non-bridged catalyst and this behaviour is in accordance with their higher crystallinity values. Fig. 2 shows the DSC endotherms obtained after step crystallization from 140 °C to 92 °C of the copolymers prepared with the silylene-bridged Me$_2$Si (Ind)$_2$ZrCl$_2$ catalyst (Cat 1). According to earlier results [2] this catalyst gave high conversions and in total 7% comonomer is incorporated into the polymer for the sample 100- 22. The homopolymer 100- 15 in the figure shows a broad peak different from the melting peaks of Ziegler-Natta (Z-N) homopolymers but no additional separated peaks are visible. This peak corresponds to a lamella thickness of about 12 nm. An increasing comonomer level however gives endotherms with up to 5 separated peaks for the highest level of incorporation. The peaks of 100-22 correspond to lamella thicknesses 13.8 nm, 10.6 nm, 6.9 nm, 5.5 nm and 4.6 nm respectively. The polymer 100-19 still shows a rather heterogeneous comonomer incorporation into the chain (strong increase in the DI numbers as function of temperature, lamella thickness range (14.2 nm–6.7 nm), but the polymers 100- 20 (lamella thickness range 13.2 nm–4.7 nm) and 100-22 show rather similar distributions of more homogeneous character. The similarity of the endotherms of 100- 20 and 100- 22 may indicate that the comonomer incorporation proceeds in about the same way when the amount of alcohol introduced is beyond a certain level.

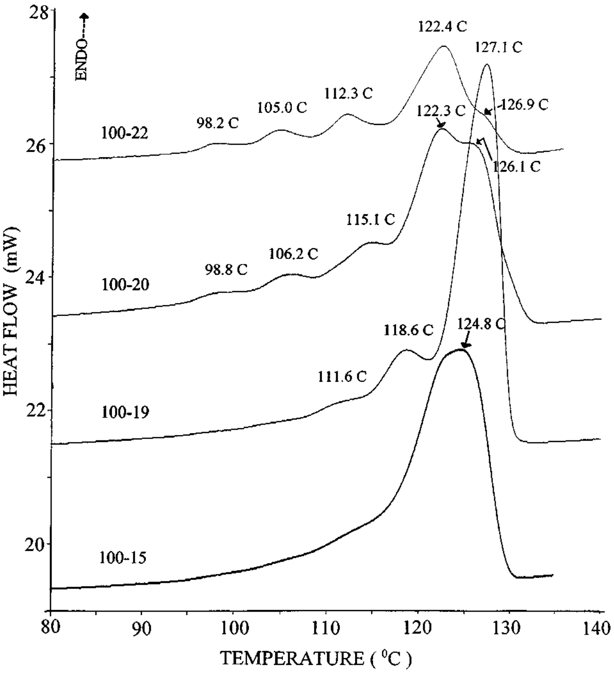


Figure 2 DSC endotherms obtained after segregation and corresponding DI values (starting from the lowest temperature) for the copolymers polymerized with silylene-bridged catalyst Cat 1 (Series 100): DI-values 0.12, 0.25 and 1 (100-19), 0.14, 0.24, 0.40, 1, 0.91 (100- 20) and 0.15, 0.26, 0.40, 1, 0.4 (100- 22).

A still more dramatic change in the endotherms after annealing is seen in Fig. 3 in the curves of polymers synthesised with the silylene-bridged catalyst Me$_2$Si(2-MeInd)$_2$ZrCl$_2$ (Cat 4) where the indenyl has a methyl group. The homopolymer shows a sharp main peak (corresponding to a lamella thickness of 21.6 nm), but increasing comonomer incorporation into the chain gives systematically less crystalline copolymer, and the copolymer 401-04 (lamella thickness range 10.8 nm–4.7 nm), containing 1.4 mol% comonomer in the chain, shows a highly homogeneous distribution (i.e. very similar DI numbers !) with no indication of the "linear" peak typical for Z-N-type ethylene -α-olefin copolymers. For this catalyst system there seems to be a dramatic change in the comonomer incorporation as the alcohol feed increases from 1.2 to 1.9 mol dm^{-2} $\times$ 10^2, and this difference is seen both in the amounts of alcohol in the polymers, 0.11 mol% and 1.4 mol% respectively, and in the different patterns of the DSC endotherms in the figure. The lower polymerization rate; that is lower ethylene consumption, using this catalyst [2] is

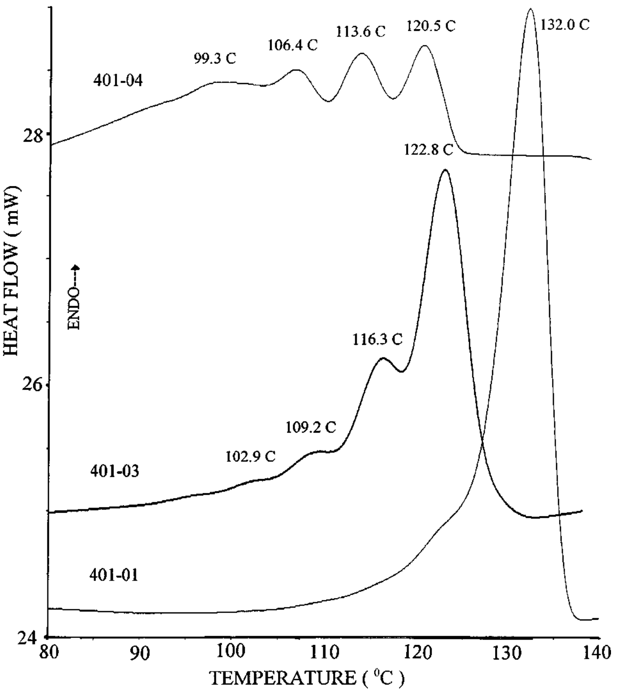


Figure 3 DSC endotherms obtained after segregation and corresponding DI values (starting from the lowest temperature) for the copolymers polymerized with silyl bridged catalyst Cat 4 (Series 400): DI values: 0.18, 1 (401- 01), 0.12, 0.20, 0.46, 1 (401- 03) and 0.77, 0.85, 0.97, 1 (401- 04).

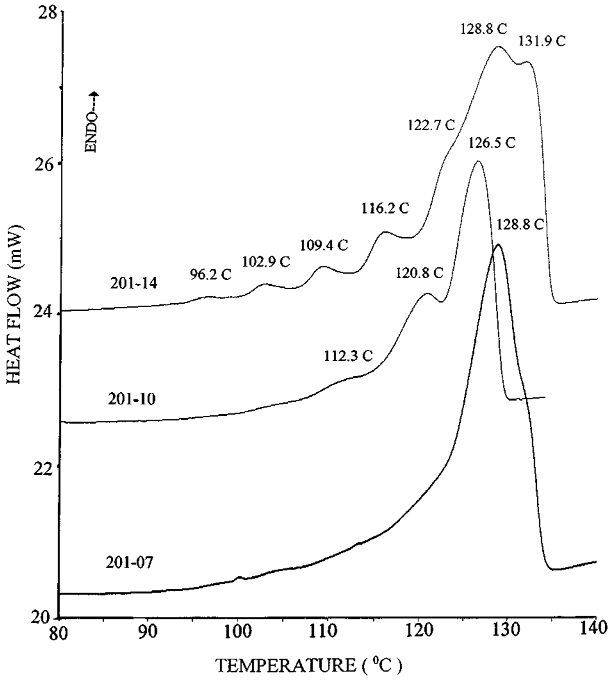


Figure 4 DSC endotherms obtained after segregation and corresponding DI values (starting from the lowest temperature) for the copolymers polymerized with the stereorigid ethylene-bridged catalyst Cat 2 (Series 200): DI values 0.17, 0.49, 1 (201- 10) and 0.05, 0.10, 0.17, 0.30, 0.56, 1, 0.94 (201- 14).

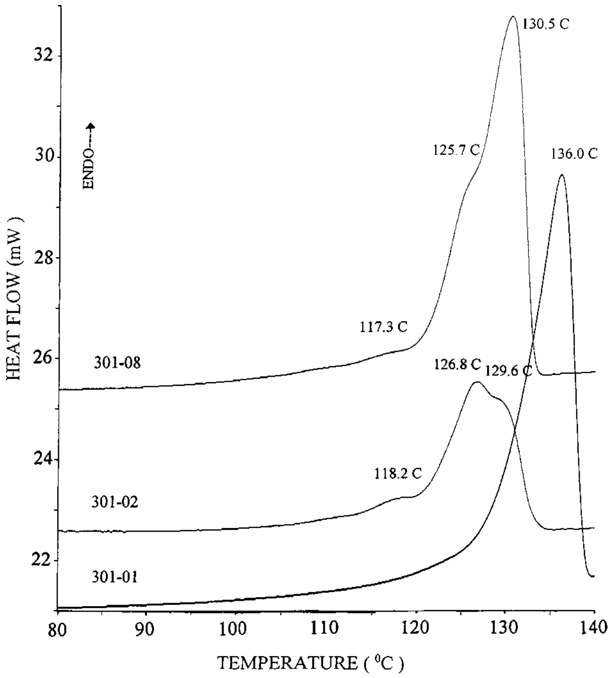


Figure 5 DSC endotherms obtained after segregation and corresponding DI values (starting from the lowest temperature) for the copolymers polymerized with the non stereospecific catalyst Cat 4 (Series 300): DI values 0.08, 0.22, 1, 0.86 (301- 02) and 0.09, 0.55 and 1 (301- 10).

the cause of this behaviour. A lower temperature range for the annealing steps of sample 401-04 had given a better separation of different crystals.

Copolymers produced with the stereorigid ethylene-bridged catalyst Et[Ind]$_2$ZrCl$_2$ (Cat 2), which gives conversions of polar comonomers only half of those obtained for the analogous silylene-bridged catalysts [2], display several separated peaks (corresponding to lamella thicknesses 21.3 nm–4.4 nm) after the annealing (Fig. 4). Still, the pattern of 201- 14 is completely different from that of 401- 04, confirming the more heterogeneous comonomer distribution of 201- 14. These differences in the step crystallization experiments are in accordance with the earlier discussed effects of comonomer incorporation effect on the melting point and crystallinity values presented in Table I.

The low comonomer conversions found for the copolymers synthesised with the non-stereospecific catalyst [Ind]$_2$ZrCl$_2$ (Cat3) are supported by the similar patterns of the curves in Fig. 5 and the very different DI numbers. Incorporation of comonomer shifts the position of the main peak from 136 °C (lamella thickness 37.7 nm) to about 130 °C, but the absence of peaks below 115 °C supports the conclusion of low conversions of comonomers for this catalyst. The ethylene segment length distribution is narrow for all copolymers (lamella thickness range 17.1 nm–8.7 nm for 301- 02) and this corresponds to a narrow comonomer distribution.

The equilibrium theory or exclusion model, describing the reduction of melting temperature, crystallinity, and crystal thickness by the presence of short chain branched repeat units, was introduced by Flory [33] over 45 years ago. According to this theory the melting temperature of a copolymer which is composed of crystallizable A units (ethylene monomers) and non-crystallizable B-units (the comonomer) will be depressed by the latter according to Flory's equation:

$$\frac{1}{T_\mathrm{m}} - \frac{1}{T_\mathrm{m}^\circ} = -\left(\frac{R}{\Delta H_\mathrm{u}}\right) \ln X_\mathrm{A} \qquad (2)$$

where ΔH_u is the heat of fusion per repeating unit of homopolymer with A units, T_m° is the melting temperature of the pure polymer, T_m is the equilibrium melting temperature of the copolymer, R is the gas constant (8.314 J/mol K) and X_A is the volume fraction of A in molten copolymer.

An effort was made to establish the equilibrium melting temperature of each copolymer by the well known Hoffman- Weeks extrapolation method [34, 35]. We determined the melting temperatures which corresponded to crystallization temperatures obtained by crystallizing the samples at the four different rates mentioned in the experimental part. As the cooling rate increased the maximum peak temperature shifted to lower temperatures. In Fig. 6 the maximum peak temperature of sample 401-04 shifts from 110.5 °C to 102.8 °C and from 116.0 °C to 111.3 °C for sample 301-08 as cooling rate increases from 5 °C/min to 30 °/min. For the polymers synthesised with Cat3 (301-series) and Cat4 (401-series) it is clearly exhibited that he nonisothermal crystallization temperature decreases as branch content increases. The 201- polymers showed a very slight decrease in peak temperature at higher crystallization rates (20 °C/min and 30 °C/min); lower rates slightly increased the peak temperatures. At higher alcohol amounts the polymers synthesised with Cat1 (100 series) also displayed lower peak temperatures with increasing branching. The melting points of all polymers studied, determined after the different crystallization experiments, changed only 0°C–1°C.

Plots of the observed melting temperatures T_m against crystallization temperatures and the extrapolated equilibrium melting temperatures T_m to the intersection with $T_m = T_c$, 45° straight line, are displayed in Fig. 7a and b. In Fig. 7a, illustrating the results of the polymers produced with the bridged catalysts 1 and 4 respectively, the equilibrium melt temperatures decrease with increasing branching, with exception of the sample 100-18 which already earlier was found to display odd melting and crystallization characteristics. Fig. 7b demonstrates, that the use of the unbridged catalyst Cat3 gives polymers where the depression effect of branching on the equilibrium melting temperatures can be noticed. In contrast to the other polymers, the 201-series (Cat 2) display nonsensical results suggesting higher T_m° numbers with increasing branching.

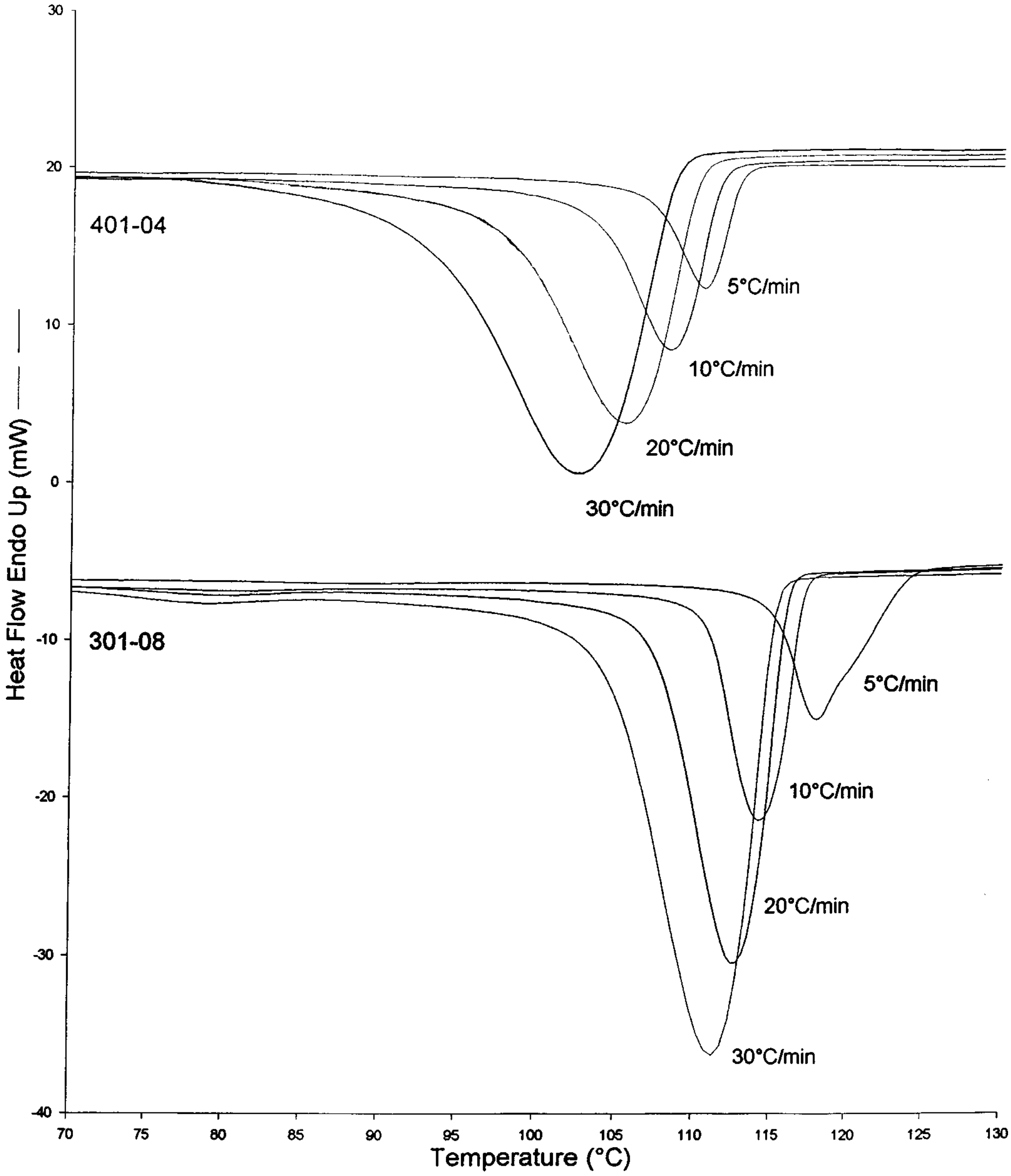
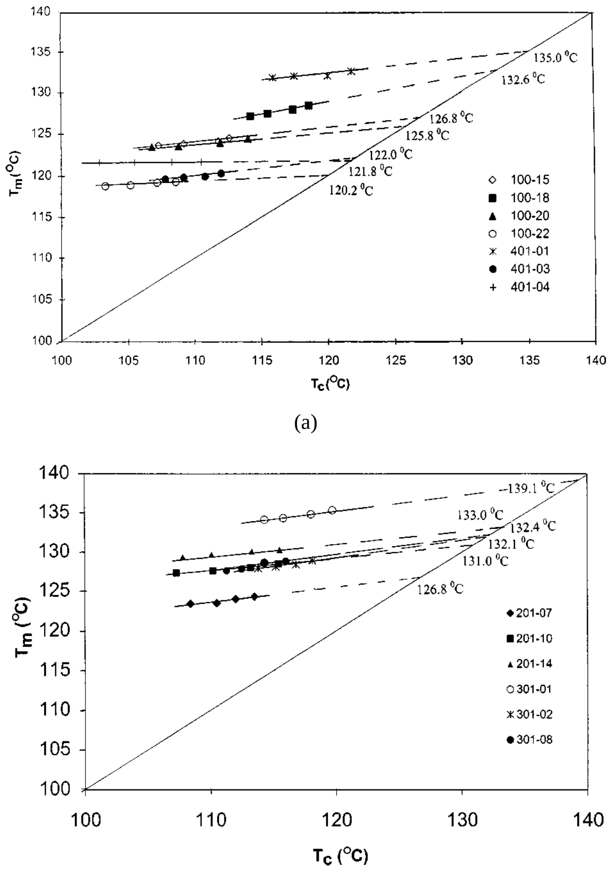


Figure 6 Nonisothermal thermograms of copolymers 301-08 (Cat3) and 401-04 (Cat4).



(a)

(b)

Figure 7 Plot of melting temperatures against crystallization temperatures. a) Series 100 and 400 b) Series 200 and 300.

Equilibrium melting temperatures calculated from theory using the Flory equation (2) with a value of $T_m^\circ = 414.5$ K (=141.36 °C) and $\Delta H_u = 4016$ J/mol and calculated X_A values from the mol% results in Table I displayed T_m numbers from 141.0 °C to 141.5 °C for all studied polymers. Thus the extrapolated melting temperatures were all lower than the theoretical expectation indicating that in the current study the copolymers are not true random copolymers as already is evident from the low melting temperature depression seen from the numbers in Table I. That the melting temperature depressions with increasing amount of comonomer in the current study were not as high as expected, based on knowledge from ethylene-α-olefin copolymers, can probably be due to the fact that the comonomers in our case are not quite randomly distributed throughout the whole polymer matrix, which also is supported both by the stepwise crystallization behaviour and by the fact that the Flory equation seems not to be valid. An other reason for this lower melting temperature depression would be caused by chain interaction through formation of hydrogen bonds between the hydroxyl groups.

The validity of the Hoffman-Weeks theory for estimation of the equilibrium melting point and the theory of Flory for the melt temperature depression due to branching has recently been discussed in publications by Alamo *et al.* [35, 36], Phillips *et al.* [37–39] and Crist *et al.* [40, 41]. The extrapolative method failed for random copolymers at low levels of crystallinity [35] and for branched ethylene-1-octene copolymers [37], displaying straight lines which are parallel to the $T_m - T_c$ line. Other investigations [38] have demonstrated, that the Flory equation can be used for ethylene-1-octene copolymers with less than 1% branch content. However, according to our knowledge the use of the Hoffman-Weeks theory and the Flory equation have not been reported for such functional ethylene copolymers studied in our work. The group of Müller [19] in their annealing studies on grafted maleic anhydride ultra low desity polyethylene suggested that a reduction of the mean lamellar thickness of their samples was promoted by the introduction of anhydride group, thus interrupting the ethylene sequences.

Alamo and Mandelkern pointed out [42] that the melting temperature of a copolymer does not depend directly on the composition but rather on the nature of the sequence distribution and a further fundamental question remains whether the co-unit does or does not enter the lattice. Moreover the contribution of molar mass has to be considered. According to the molar masses and molar mass distributions exhibited in Table I the molar mass is decreasing with comonomer incorporation for all polymers studied, suggesting a partial incorporation of comonomer in the chain.

3.2. DMA measurements

The relaxation behaviour of polyethylene is strongly influenced by variables that describe the crystalline state, such as crystallinity and lamellar thickness. The α relaxation, observed between +20 °C and +70 °C, is related to the crystalline phase. A decrease in the temperature of the α relaxation with decreasing lamellar thickness is generally noticed [43]. The β transition at about 0 °C to −30 °C is attributed to the amorphous regions because its magnitude increases with decreasing crystalline fraction. Both the α and the β transitions are strongly affected by comonomer content for ethylene-α copolymers. The storage modulus (E') values at 25 °C obtained from DMA-measurements of the copolymers are shown in Table I. E' is approximately equal to the Young or elastic modulus or stiffness [20] and according to Nunnery [44] the storage modulus indeed agrees closely with flexural modulus as measured by ASTM D 790. As indicated by the storage modulus numbers, the stiffness levels are slightly higher or at least at the same level for the copolymers as for the corresponding homopolymers. Fig. 8 shows the modulus curves and loss tangent curves of the polymers synthesised with the bridged $Me_2Si(Ind)_2ZrCl_2$ catalyst (Cat1). Curves are the calculated averages of duplicate runs. Over most of the temperature ranges studied the copolymers showed slightly higher modulus than the homopolymer (Table I), but there was no direct correlation with the comonomer content. Still smaller differences in the modulus values were seen (not shown) for the other polymer families, the 301 and 401 series, synthesised with other catalysts. From this it can be concluded that copolymerizations of ethylene with 10-undecen-1-ol will not weaken the stiffness levels of the polymers. Surprisingly, despite the rather big differences in the crystallinity values of the different 401- polymers

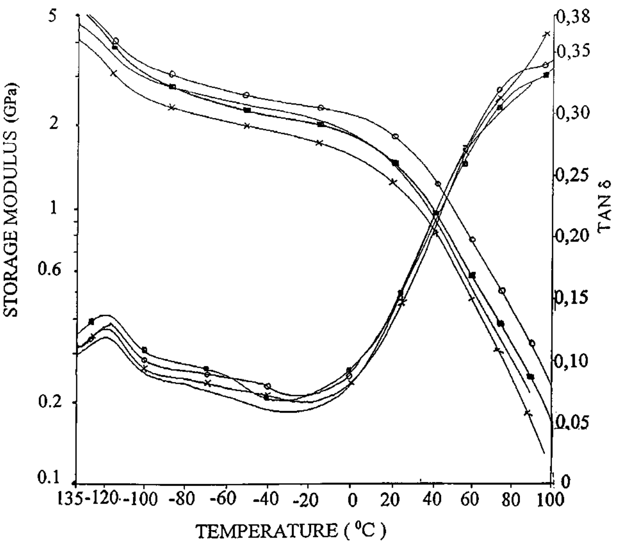


Figure 8 Storage modulus and loss tangent curves of ethylene-10-undecene-1-ol copolymers 100- 18 (symbol ○), 100- 19 (no symbol), 100- 20 (symbol ●) and corresponding homopolymer 100- 15 (symbol x), all produced with bridged catalyst Cat 1.

in Table I they do not display any differences in the modulus curves. The choice of catalyst system will not either have any significant influence on the mechanical properties. The β-relaxation does not exhibit any tan δ peak corresponding to presence of branching. Same behaviour existed for the 301-polymers (unbridged catalyst) and 401-polymers (bridged catalyst). Although the step crystallization experiments indicated that some of the synthesised copolymers, such as 401-03 and 401-04, consist of shorter ethylene sequences, the DMA-measurements demonstrate that the polymers investigated obviously consist of lamellae and severely constrained lamellar boundary regions.

4. Conclusions

The introduction of metallocene catalysts has vastly widened the possibilities for copolymerizing ethylene with bulkier monomers. In this work the comonomer distributions in copolymers of ethylene with 10- undecen-1-ol were analyzed by DSC using stepwise crystallization by annealing at different temperatures and by performing nonisothermal crystallization at different rates. DMA analyses were performed in order to get an impression of the mechanical properties of the synthesised copolymers.

The studies on the functional copolymers showed that a separation into different lamellar populations takes place during stepwise crystallization. This behaviour is based on differences in the ethylene chain length of the copolymers. The broadness of DSC endotherms, obtained after annealing steps, and the sizes of the separated peaks give more detailed information on the comonomer incorporation into the chain than the DSC endotherms of unannealed samples. The results also showed that, after segregation, polymers synthesised with bridged catalysts give endotherms with many resolved peaks and fairly homogeneous comonomer distribution. This was especially true for the copolymers prepared with the silylene-bridged catalyst.

An increased branch (i.e. defect) incorporation resulted in clear but rather weak lowering of the non-isothermal crystallization temperatures. By using the Hoffman-Weeks extrapolation of melting point vs crystallization temperature reasonable equilibrium melting temperatures were obtained for the polymers produced with the silylene bridged catalysts. The extrapolated melting temperatures were all lower than the theoretical values obtained from the Flory equation. The relative low melting temperature depressions with increasing amount of comonomer may be due to the fact that the comonomer is not randomly distributed throughout the whole polymer matrix or that a chain interaction through formation of hydrogen between the hydroxide groups takes place. For this type of copolymers small-angle-light-scattering (SAXS) and electron microscopy measurements may give valuable information concerning the exclusion of branches from the crystalline phase.

DMA measurements on the functional copolymers were possible after homogenization of the samples in a midiextruder and preparation of the DMA specimen in a moulding device attached to the midiextruder. Study of the storage modulus curves showed that the flexural modulus properties will remain or be slightly improved if 10-undecen-1-ol is incorporated in the chain. The damping curves do not indicate any presence of comonomer although. Apparently the alcohol is only interrupting the ethylene sequence to a slight extent although differences in the comonomer distributions were seen from the DSC measurements.

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