Copolymerization and Characterization of Ethene–1-Hexene Copolymers Prepared by Using the (Me₅Cp)₂ZrCl₂–MAO Catalyst System

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ABSTRACT: It is demonstrated that the catalyst system bis(pentamethylcyclopentadienyl)-zirconium dichloride (Me_5Cp)₂ZrCl₂-methylaluminoxane (MAO) is able to produce random copolymers of ethene and 1-hexene. The 1-hexene incorporation in the copolymers is extremely small. Even in the case of a molar ratio of [ethene] to [1-hexene] of 1/20 in the monomer feed, only 1.4 mol % 1-hexene are incorporated according to ¹³C nuclear magnetic resonance (NMR) spectra. Nevertheless, the physical properties of the random copolymers change significantly in this small range of 1-hexene incorporation, from a high-density polyethene to a linear low-density polyethene. Thus, the melting temperature, the degree of crystallinity, the density and lamella thickness, and the long period of the alternating crystalline and amorphous regions decrease with increasing 1-hexene content in the random copolymers. Blends of high-density polyethene prepared with the system (Me_5Cp)₂ZrCl₂-MAO and an elastomeric random copolymer of ethene and 1-hexene are phase-separated and show good compatibility, as demonstrated by transmission electron microscopy. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 439-447, 1999

Key words: metallocene catalysts; polyethene; ethene-1-hexene copolymers; blends

INTRODUCTION

There has been a tremendous development in the olefin polymerization in recent years mainly based on the introduction of single-site metallocene catalysts activated by strong Lewis acids.^{1–8} These homogeneous Ziegler catalysts are usually formed by the reaction of group (IV) metallocenes and methylaluminoxane (MAO). Copolymers of ethene with higher α -olefins produced by these

new catalyst systems are meanwhile well-established commercial products with an application spectrum ranging from linear low-density polyethene (LLDPE) to thermoplastic elastomers (plastomers) and rubber.^{9–13} The copolymerization behavior of ethene with other α -olefins depends strongly on the catalyst architecture.^{14–18} In contrast to conventional multisite Ziegler catalysts, it is possible to produce random copolymers over the entire composition range or nearly neat polyethene. Placing a blend of single site catalysts on a metal oxide support thus generates the possibility of the *in situ* production of reactor blends in a gas phase process. This is based on the

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suitable selection of catalysts, which are able to produce simultaneously and independently, on the one hand, high-density polyethene as a matrix polymer and, on the other hand, an ethene– α -olefin random copolymer as an elastomer in the dispersed phase, respectively.

The relatively small reactivity of the comonomer during the copolymerization of ethene with propene¹⁹ or 1-hexene²⁰ using the catalyst system (Me₅Cp)₂ZrCl₂-MAO makes it suitable for the preparation of high-density polyethene in the presence of α -olefins. Nevertheless, it is important to study the influence of the presence of a comonomer on the polymerization behavior of this catalyst system. This contribution deals with the copolymerization of ethene and 1-hexene using the catalyst system described above and with the crystallization behavior of the respective random copolymers studied by differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS), and small-angle X-ray scattering (SAXS). Furthermore, polymer mixtures are prepared by solution blending a high-density polyethene synthesized, as described above, and an elastomer. The elastomer is a random copolymer of ethene and 1-hexene containing 17.2 mol % 1-hexene prepared by using the catalyst system ethylene bis(indenyl) zirconium dichloride C₂H₄(Ind)₂ZrCl₂-MAO.

EXPERIMENTAL METHODS

Materials

All catalyst components, including the solvent toluene and monomers, were handled and stored under dry argon atmosphere. (Me₅Cp)₂ZrCl₂ (99 wt %, Strem Chemicals) was sublimated at 110°C and 7.3 \times 10⁻⁶ bar. C₂H₄(Ind)₂ZrCl₂ was obtained by Witco and it was used as obtained without further purification. Toluene (99.8 vol % HPLC grade, Aldrich) was stored and distilled over CaH₂ and refluxed over Na-K-alloy, from which it was freshly distilled prior to use. 1-Hexene was stored and distilled over CaH₂ with tri*n*-butylaluminium (0.1 vol %) and it was freshly distilled prior to use. Ethene (99.5 vol %, Messer Griesheim GmbH) was purified by passing it through two columns with a 0.4-nm molecular sieve (Zeosorb 4A S3) and one column with Leuna catalyst (Copper contact 4492, LEUNA Werke AG).

Copolymerization and Catalyst Preformation

All products were transferred through a syringe under argon atmosphere at 25°C in a 1000-mL stainless steel autoclave (Büchi, Switzerland) equipped with an efficient stirrer operating at 1000 rpm. The reactor was filled with toluene, 1-hexene, and a part of the MAO needed. After thermostating the reactor, the reaction mixture was saturated with ethene for 1 h. The polymerization experiments were performed in the presence of a preactivated catalyst. In a 50-mL Schlenk flask the metallocene solution, and $\frac{2}{3}$ of the total MAO solution was prereacted for 20 min. The metallocene-MAO solution was then injected into the reactor flask so that an *in situ* start of the copolymerization was achieved. The ethene pressure was kept constant during the polymerization and the consumption of the monomer was recorded via pressure measurements. Further polymerization conditions are reported in Table I. The copolymerizations were stopped by injection of 10 mL of methanol and venting off the excess of ethene. The copolymers were washed with a solution of hydrochloric acid (2 vol %)-water (49 vol %)-methanol (49 vol %) to remove residues of the catalyst and the cocatalyst. Finally, the copolymers were filtered and dried under vacuum to constant weight.

Polymer Characterization

¹³C nuclear magnetic resonance (NMR) measurements were performed at 140°C with an acquisition time of 3.2 s, a pulse width of 90°, and a pulse delay of 10 s on a VARIAN UNITY 400 at 100.5 MHz. Samples of 200 mg of polymer were dissolved in 1.25-mL 1,2,4-trichlorobenzene in a 10mm-o.d. tube. 0.75 mL of 1,1,2,2-tetrachloroethane-d₂ was added as an internal lock. Signals were assigned according to the literature.²¹

Molar masses and molar mass distributions reported were determined by high-temperature size exclusion chromatography (Knauer) (135°C; 1,2,4-trichlorobenzene) with an universal calibration function $[\log (Mx[\eta]) = f$ (elution volume)] in connection with a Kuhn–Mark–Houwink equation.²²

Differential scanning calorimetry (DSC) was performed on a Seiko DSC 220. Each sample was heated from 25 to 160°C at a heating rate of 20°C/min and kept at this temperature for 5 min. It was then cooled to -140°C at a rate of 2.5°C/ min and reheated with 20°C/min. The melting

Run 1-Hexene 1-Hexene <th< th=""><th></th><th></th><th></th><th>1 Hornon Contout</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></th<>				1 Hornon Contout							
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Run	1-Hexene ^b	1-Hexene (mol/L)	1-revene Content in the Copolymer ^e (mol %)	Density ^d (g/cc)	Crystallinity ^e (%)	T_m^{f} (°C)	$M_n imes 10^{-3\mathrm{g}} \ \mathrm{(g/mol)}$	M_w/M_n	$A_{ m Cat} imes 10^{-6{ m h}}$	[Zr] (µmol/L)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	P(E-co-H)1/0	0	0	0	0.951	69.6	140	69.7	5.2	3.2	10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	P(E-co-H)1/1	1	0.2	Ι	0.937	60.4	135	65.9	5.2	5.8	10
$ \begin{array}{ccccccc} {\rm P(E-co-H)1/3} & 3 & 0.6 & - & 0.931 & 56.3 & 130 & 255.0 & 2.5 & 11. \\ {\rm P(E-co-H)1/4} & 4 & 0.8 & - & 0.930 & 55.6 & 127 & 102.0 & 3.1 & 8. \\ \end{array} $	P(E-co-H)1/2	2	0.4	Ι	0.936	59.7	132	91.7	2.7	11.8	10
P(E-co-H)1/4 4 0.8 — 0.930 55.6 127 102.0 3.1 8	P(E-co-H)1/3	က	0.6	Ι	0.931	56.3	130	255.0	2.5	11.6	ŋ
	P(E-co-H)1/4	4	0.8	Ι	0.930	55.6	127	102.0	3.1	8.4	10
P(E-co-H)1/8 8 1.7 0.4 0.926 52.9 122 82.9 2.4 9.	P(E-co-H)1/8	80	1.7	0.4	0.926	52.9	122	82.9	2.4	9.9	10
P(E-co-H)1/20 20 4.0 1.35 0.912 4.3.1 117 129.0 2.6 9.	P(E-co-H)1/20	20	4.0	1.35	0.912	43.1	117	129.0	2.6	9.9	ŋ
Elastomer ^a 4 0.8 15.4 0.876 16.9 33.4 47.6 2.3 3.	${ m Elastomer}^{ m a}$	4	0.8	15.4	0.876	16.9	33.4	47.6	2.3	3.6	5

 Table I
 Copolymerization of Ethene with 1-Hexene Using (Me₆Cp)₂ZrCl₃-MAO

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temperature data were taken from the second scan.

The samples for SAXS measurements were placed in a hot press at 225°C for 15 min at normal pressure. Then a pressure of 80 kbar was applied for 2 min at this temperature. The bars were then placed in another press at room temperature and kept for 5 min at 30 kbar. The bars with a thickness of 2 mm were placed in an evacuated Kratky compact camera (PAAR, Austria). The CuK_{α} radiation of a wavelength $\lambda = 0.154$ nm was used. The scattered intensity I was recorded by a scintillation counter in a step-scanning mode at room temperature. The scattering profiles were corrected for background scattering and desmeared. The Fourier transformation of the scattering curve yields the linear correlation function K(z) defined by^{23,24}

$$K(z) = \int_0^\infty 4\pi s^2 I(s) \cos^2 \pi s z \ ds \tag{1}$$

where s is the scattering vector given by $(2/\lambda)\sin(\Theta/2)$ and Θ is the scattering angle.

The precipitated samples for wide-angle X-ray scattering (WAXS) measurements were dried, and the powder was heated up to 200°C for 2 min and then isothermally crystallized at 60°C for 1 h. The WAXS measurements were carried out with a Seifert XRD 3000 PTS apparatus using CuK_{α} radiation. The scans were taken between 5 and 35° in intervals of 0.1°.

 $\times \text{ mol}_{\text{metallocene}} \times h_{\text{polymerization time}})].$

ratio in the monomer feed.

Determined with ¹³C-NMR spectroscopy.

1-Hexene]/[ethene]

Bulk density of polymer film

Calculated from density using literature data. Determined by DSC with 20°C/min.

From size exclusion chromatography

monomer $_{
m units})/(
m mol/L)$

inserted ethene

[(Mol

The blend was prepared by dissolution of P(Eco-H)1/4 (80 wt %) and the elastomer (20 wt %) in *p*-xylene at 135°C, followed by precipitation in cold methanol. The blend was dried under vacuum at room temperature to constant weight.

Ultrathin sections of the P(E-co-H)1/8 sample and of the blend of P(E-co-H)1/4 with the elastomer for transmission electron microscopy (TEM) were prepared with an ultramicrotome (Ultracut E, Reichert & Jung). They were stained by RuO₄ in the gas phase. The TEM apparatus was a JEM 2010 operated with an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Ethene was copolymerized with 1-hexene at 25° C in toluene in the presence of MAO preactivated (Me₅Cp)₂ZrCl₂ using an [Al]/[Zr] ratio of 1800



Figure 1 ¹³C-NMR spectra of P(E-co-H)1/8 and P(E-co-H)1/20.

over the whole monomer feed composition range. The solubility of ethene in toluene–MAO and in a mixture of toluene–1-hexene–MAO at 25°C and an ethene pressure of 1.47 bar are determined according to the literature.²⁵ The ethene concentration is [ethene] = 0.2 mol/L in agreement with the data of Schneider.²⁵ Experimental results and reaction conditions of the ethene–1-hexene copolymerization experiments are summarized in Table I.

Catalyst molar activities $(A_{\rm Cat})$ of copolymerization reactions were calculated according to

$$A_{\text{Cat}} = \frac{n_{\text{ethene}}}{[\text{ethene}] \cdot n_{Zr} \cdot t_P}$$
(2)

taking into account the total number of inserted ethene monomers n_{ethene} per mole of transition metal of $(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$, n_{Zr} . [Ethene] is the molar concentration of ethene in the monomer feed, and t_P is the polymerization time. The incorporation of 1-hexene in the copolymer is calculated according to ¹³C-NMR spectra, which are shown for P(E-co-H)1/8 and P(E-co-H)1/20 in (a) the original spectra, (b) the fit to the original spectra, and (c)–(e) the peaks assigned to the different sequences taken for fitting the spectrum in the range from 23 to 43 ppm in Figure 1. The resonances are assigned according to the scheme of Hsieh and Randall.²⁶ We have used the numerical procedure reported by Cheng²¹ to calculate the copolymer composition. At lower 1-hexene incorporations compared to the two samples discussed above, the direct determination of copolymerization parameters from ¹³C-NMR data is not possible due to low intensity of significant ¹³C-NMR signals.

Table II shows the values for the copolymerization parameters of ethene obtained by using the method of Böhm, which takes into account the copolymer composition.²⁷ A quantitative determination of the ethene content by ¹³C-NMR data is only possible for these two copolymers. By comparing the values of r_{ethene} for the copolymers, it can be seen that the (Me₅Cp)₂ZrCl₂ preferentially incorporates ethene since the r_{ethene} value is very high and the corresponding $r_{1-\text{hexene}}$ value is close to 0. These values confirm that the formation of 1-hexene blocks in the copolymer is very unlikely.

Table II $r_{\rm ethene}$ Values Obtained from TwoCopolymers Using the Method of Böhm27

Polymer	$r_{ m ethene}$
P(E-co-H)1/8	1990
P(E-co-H)1/20	1460

The preference of ethene incorporation with respect to 1-hexene is clearly visible. Therefore, it is possible to use this catalyst system for the synthesis of a matrix material in reactor blends with a very low comonomer incorporation.

Table I shows the dependence of the catalyst molar activity on the [ethene]/[1-hexene] ratio in the polymerization solution. Starting from the ethene homopolymerization, the catalyst molar activity increases considerably with an increasing [1-hexene]/[ethene] ratio until a ratio of 2 is reached. At this ratio, the catalyst molar activity is 3.7 times more than the homopolymerization activity of ethene. This acceleration effect of a higher α -olefin seems to be a general phenomenon of the ethene- α -olefin copolymerization with Ziegler catalysts.²⁸⁻³¹ At a [1-hexene]/[ethene] ratio greater than 2, we observed that the catalyst molar activity is constant. With the methylaluminoxane activated catalyst system, the activity reducing effect of α -olefins, which should increase with increasing 1-hexene concentration, must be overcompensated by an additional activity enhancing effect, which might be the better solubility of the polymer or a change of the coordination at the active center of the catalyst.

It is well known that the molar mass of any polymer is determined by the ratio of the rate of the propagation reaction to the sum of the termination and chain transfer reactions. For the

(Me₅Cp)₂ZrCl₂–MAO catalyst system, there is an increase in the molecular weight of the copolymers at very low 1-hexene contents in the copolymer caused by the molecular weight enhancing effect since the effect of the strongly increased ethene activity is greater than the molecular weight reduction effect caused by the β -H elimination reaction of the active species (polymer-CH(R)-CH₂-cat)³² or by the chain transfer reaction with 1-hexene. The observed increase in the molecular weight of the ethene-1-hexene copolymers up to very high 1-hexene amounts in the monomer mixture is difficult to understand up to now. It should also be mentioned that there is a significant influence of the catalyst concentration on the molar mass. In the case of a catalyst concentration of 5 μ mol/L, the molar mass is obviously higher compared to the polymers prepared with a catalyst concentration of 10 μ mol/L. The molar mass distribution of the polyethene homopolymer and the copolymers with small amounts of 1-hexene is higher than that expected for single site catalysts $(M_w/M_n$ should be in the range of about 2). This may be due to dynamic dissociation/association of MAO and changes in its state of coordination.³³ Another possible cause for the high polydispersity may be the competitive coordination of α -olefin, ethene, and toluene at the coordinatively unsaturated cationic zirconium atom.34



Figure 2 DSC traces of polyethene and different P(E-co-H) copolymers. The data are taken with a heating rate of 20°C/min.



Figure 3 WAXS traces of P(E-*co*-H)1/0, P(E-*co*-H)1/2, P(E-*co*-H)1/4, and P(E-*co*-H)1/20.

After knowing that the incorporation of 1-hexene into the copolymers is extremely small, it is highly interesting to study the influence of these small comonomer contents on the solid state properties of the respective copolymers. The DSC heating traces for the polyethene homopolymer and the copolymers obtained using the $(Me_5Cp)_2ZrCl_2$ -MAO catalyst system for different [ethene]/[1-hexene] ratios in the feed are shown in Figure 2. It can be seen that the minimum of the melting peak shifts towards lower temperatures

with increasing amounts of α -olefin in the monomer mixture. It is surprising that this enormous shift is reached with a maximum incorporation of 1.4-mol % 1-hexene in the random copolymer (P(E-co-H)1/20). Table I summarizes the decreasing melting temperatures and crystallinities with increasing amounts of 1-hexene in the copolymer. The incorporation of a very small amount of a higher linear α -olefin leads to short chain branches randomly distributed in the polymer backbone. The short chain branching lowers both crystallinity and density. The broadening of the melting peak found for higher contents of 1-hexene in the copolymer can be due to factors like the different size of crystals and imperfections in the crystalline lattice.

The small amounts of comonomer incorporated in the copolymer have also a significant influence on the crystallization behavior. The WAXS measurements shown in Figure 3 indicate a decrease of the degree of crystallinity with increasing comonomer content in the copolymers in agreement with DSC data. For copolymers with considerable 1-hexene incorporation the ratio of the area of Bragg reflection to the amorphous halo decreases. There is not any significant shift in the peak position, as expected for these small amounts of comonomer contents, no matter if the comonomer units are excluded from the crystal



Figure 4 Absolute, desmeared scattered intensity *I* of different P(E-*co*-H) samples as a function of the scattering vector *s*. The three upper graphs are shifted by a factor of 10, 100, and 1000, respectively. The inset is a plot of Is^2 versus *s*.



Figure 5 One dimensional correlation functions K(z) for different P(E-*co*-H) samples. The two upper graphs are shifted by 200 and 400 eu²/nm⁶, respectively. The inset shows a TEM micrograph of lamellae of the copolymer P(E-*co*-H)1/8.

lattice or not. Because all samples had the same thermal history, these small comonomer contents are obviously sufficient in order to reduce the rate of crystallization considerably.

The influence of the comonomer incorporation on the lamella thickness and the long period can be obtained from small-angle X-ray scattering (SAXS) measurements. Figure 4 shows the desmeared SAXS data, and the inset represents the Is^2 versus *s* plot. The data show a significant peak (most pronounced for the Is^2 versus s plot) for all three copolymers at s^* . A shoulder can be observed between $3s^*$ and $4s^*$ as a result of higher order peaks. They are indicated by arrows for the example of P(E-co-H)1/2. This shoulder might be the result of incomplete resolution of the two respective reflections. The absence of the second order peak can be explained when the amorphous and crystalline regions have similar dimensions.³⁵ The maximum for neat polyethene (P(Eco-H)1/0) is obviously very close to the beam stop $(s < 0.02 \text{ nm}^{-1})$ and it cannot be evaluated quantitatively. But there is an inflection point in the trace, indicating a possible peak. Thus, the linear

correlation function K(z) is calculated only for the three copolymers (see Fig. 5). Assuming alternating crystalline and amorphous regions (stacks of lamella), it is possible to obtain the long period from the first maximum.³⁷ It can be seen that the long period decrease with increasing 1-hexene content in the copolymer. The long period for P(Eco-H)1/0 should be larger than 38.5 nm, and it decreases to 23.1 nm for P(E-co-H)1/2, to 18.7 nm for P(E-co-H)1/4, and to 15.2 nm for P(E-co-H)1/420. It is also possible that the lamella thickness decreases with increasing 1-hexene content. But for a quantitative data evaluation, the correlation function is not possible because a plateau region in the range of the first minimum does not appear, and the slope of the correlation function at small z-values is not linear. The intersections [(a)-(c)] shown in Figure 5 are thus somewhat arbitrary. But taking into account the fact that the melting points decrease with increasing 1-hexene content of the copolymers, as discussed above, it seems to be reasonable to conclude from the respective correlation functions that the lamella thickness decreases too.

a)



Figure 6 TEM micrographs of two different magnification of the blend system P(E-co-H)1/4 and rubber. Magnification (a) $\times 10$ K and (b) $\times 50$ K.

As already mentioned, the shape of the correlation functions in the Porod region is different from that expected from ideal stacks of lamella with alternating regions of higher and lower electron density (responsible for the contrast in X-ray scattering). A possible reason for the deviations is shown in the electron microscopic observation of lamellae of P(E-co-H)1/8 shown in the inset of Figure 5. The lamellae are clearly bent, which might be the reason for the nonlinear slope of the correlation function in the small z-rage. Also, an extended interphase between amorphous and crystalline regions with a gradual change of the electron density is a possible reason for the observed shape of the correlation functions.

As discussed in the introduction, the final goal of these studies is the preparation of reactor blends, that is, rubber toughened polyethenes. In a first step, we prepared solution blends of P(E*co*-H)1/4 with the rubbery copolymer of ethene and 1-hexene containing 17.2 mol % 1-hexene. This rubber was synthesized under identical conditions as the matrix material, except that a different catalyst system was used. This catalyst system $C_2H_4(Ind)_2ZrCl_2$ -MAO is able to incorporate large amounts of α -olefins when copolymerized with ethene.^{33,38} Thus, a mixture of both catalyst systems may be suitable to form the respective reactor blends. Figure 6 shows TEM mi-

crographs of the solution blends of P(E-co-H)1/4 with the elastomer (80/20 wt %). In the lower magnification TEM micrograph [Fig. 6(a)], it is clearly visible that both polymers are immiscible, and a two-phase morphology is formed. This morphology with the dispersed rubber phase (dark spots) might be suitable for rubber-toughened polyethene. The higher magnification micrograph [Fig. 6(b)] depicts the growth of the crystalline lamellae in more detail. The lamellae originate in the matrix material, and they grow deeply into the rubber phase. There does not exist any indication of a sharp phase boundary. Thus, it can be assumed that both polymers, that is, the highdensity polyethene matrix and the dispersed rubber, have good compatibility. This might result partially from the small amount of 1-hexene incorporated into the matrix material because the repulsive interaction in random copolymer blends of the type AB/AB are lowered compared to the respective blends of the system AB/A.³⁹

CONCLUSIONS

It is demonstrated that the catalyst system $(Me_5Cp)_2ZrCl_2$ -MAO is able to produce copolymers of ethene and 1-hexene. The incorporation of 1-hexene is extremely small and occurs only in

the presence of a large excess of 1-hexene in the monomer feed. Therefore, this catalyst is a suitable candidate for the preparation of reactor blends when a second catalyst is added to the support that allows for incorporation of large amounts of 1-hexene into the copolymer leading to an elastomer phase. Furthermore, it is shown that very small amounts of copolymer units have a tremendous effect on the crystallization behavior. Finally, first results on solution blends of copolymers with an extremely small amount of 1-hexene and a rubber indicated that there is a good compatibility. Thus, it seems possible that toughened reactor blends can be prepared by metallocene catalyst blend systems in the presence of ethene and α -olefins in which one catalyst incorporates nearly exclusively ethene and the other catalyst forms random copolymers of ethene with large amounts of α -olefins.

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