The Production of Ethene/Propene/5-Ethylidene-2-Norbornene Terpolymers Using Metallocene Catalysts: Polymerization, Characterization and Properties of the Metallocene EPDM

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ABSTRACT: Metallocene catalysts $Et(Ind)_2ZrCl_2/MAO$ and $Et(Ind)_2HfCl_2/MAO$ were used in ethene/propene copolymerization and in ethene/propene/5-ethylidene-2-norbornene (E/P/ENB) terpolymerization. The copolymerization activity of the $Et(Ind)_2ZrCl_2/$ MAO system was 20×10^3 $kg_{polym}/mol_{Mt}*h$, the $Et(Ind)_2HfCl_2/MAO$ yielding 5×10^3 $kg_{polym}/mol_{Mt}*h$. The polymerization activity decreased with diene addition, but this effect was significant only at very large diene feeds. The catalysts incorporated diene readily. Materials with an ethene content of 55 to 70 mol % and an ENB content of 2 to 16 mol % were produced. $Et(Ind)_2HfCl_2$ produced a considerably higher molar mass material than the $Et(Ind)_2ZrCl_2$ catalyst. The molar mass distributions were narrow. Copolymers and terpolymers with up to 3 mol % ENB content had some crystallinity. Copolymer T_gs were between $-59°C$ and $-55°C$. The terpolymer glass transition temperature rose $1.5°C$ per wt % of ENB in the polymer. Polymer characteristics reported include composition, molar mass distribution, melt flow rate, density, and thermal behavior. The dynamic mechanical and rheological properties of the materials in comparison with commercial E/ P/ENB terpolymers are discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 35–44, 1997

Key words: ethene/propene/diene terpolymerization; metallocene catalyst; olefin terpolymerization; metallocene EPDM

INTRODUCTION

Ethene/propene copolymers and terpolymers with dienes, referred to as EPDM rubber, are currently produced with vanadium-based catalysts. The vanadium-based catalysts are low in yield and, furthermore, the diene concentration in polymerization is limited due to side reactions.[1] Recently, the reduction of vanadium in the presence of linear and cyclic dienes was reported to be the cause of low terpolymerization activity.[2] At the same time, research into metallocene-based catalysts for olefin polymerization has been intensive.[3] The driving force for this interest has been the new properties of the polymers produced with these catalysts. The suitability and behavior of metallocene/MAO catalysts in the terpolymerization of ethene, propene, and diene has been evaluated in several articles. The termonomers employed include ethylidene norbornene,[4–8] 4-vinylcyclohexene, and cyclooctadiene,[9] linear 1,4-hexadiene,[10] and 1,5-hexadiene.[11] The aim of this article is to extend the characterization of the metallocene-produced EPDM to properties that allow for the evaluation of their processability-related properties with reference to conventional EPDM. For this, metallocene catalysts $Et(Ind)_2$-

$ZrCl_2$/MAO and $Et(Ind)_2HfCl_2$/MAO were employed for ethene/propene copolymerization and ethene/propene/5-ethylidene-2-norbornene (E/P/ENB) terpolymerization. Besides polymerization activity and polymer composition, melt flow rates, density, and thermal behavior of the materials were determined. The viscoelastic properties of the metallocene polymers in comparison to commercial E/P/ENB terpolymers were evaluated with DMA and dynamic rheological experiments.

EXPERIMENTAL

Polymerization

All the chemicals used were obtained from commercial sources. The catalysts and methylaluminiumoxane MAO (10 wt % solution in toluene) were purchased from Witco. 99% 5-ethylidene-2-norbornene (5-ethylidene-bicyclo[2.2.1]hept-2-ene) was purchased from Aldrich. It was a mixture of *cis*- and *trans*-isomers, containing 80% of the *cis* form. It was dried with molecular sieves, then bubbled with nitrogen. Ethene and propene were purified by passing them through columns containing molecular sieves, Cu, and Al_2O_3. Polymerizations were done using the semiflow method reported by Lehtinen.[12] The combined gas flow rates were 2 or 4 NL/min. The flow ratios of gases were determined with mass flow meters. Ethylidene norbornene (ENB) was fed batchwise. A slight concentration change occurred over the reaction time because of the batchwise addition of the termonomer. Polymerizations were run in 250 mL toluene at 40°C. The polymerization pressure was 3 bar. The catalyst amount in polymerization was 0.5 mg of $Et(Ind)_2ZrCl_2$. $Et(Ind)_2HfCl_2$ was used in 2 mg amounts. MAO was used as cocatalyst, using Al/Mt ratios of 3000 or 4500 for the Zr catalyst and 6000 for the Hf catalyst. Polymerizations were run for 30 min. All the diene containing polymers were soluble in toluene at 40°C. The polymers were precipitated with HCl/acetone and washed with ethanol. The polymers were dried under reduced pressure at 50°C for 20 h. The monomer conversions were generally less than 10%, but conversions were higher for the most active $Et(Ind)_2ZrCl_2$/MAO-catalyzed polymerizations.

Product Characterization

The ethene and propene content of both co- and terpolymers was calculated from ^{13}C-NMR spectra according to the method presented by Kaguko et al.[13] The diene content was determined by ^{1}H-NMR. The molar mass distribution of the polymers was determined with a Waters high-temperature GPC instrument 150C, at 140°C using 1,2,4-trichlorobenzene as solvent. The flow rate was 1 mL/min. The columns were calibrated with narrow molar mass distribution polystyrene samples. The molar masses were calculated using the Mark-Houwink parameters for polyethene. No corrections for co- and terpolymer composition were made.

The DSC measurements were carried out with a Perkin−Elmer DSC-7 instrument calibrated with indium and water. To study the copolymer crystallization, the samples were heated to 180°C, kept there for 1 min, then cooled to 0°C and reheated to 180°C at a rate of 10°C/min. The terpolymer samples were first heated to 180°C, then cooled to −75°C at a rate of 20°C/min. They were kept at −75°C for 1 min, then heated to 150°C at 20°/min. The crystallization and melting curves were recorded.

Melt flow rates were determined at 125°C, high molar mass copolymers at 190°C with CEAST modular flow equipment. Material density was determined in a density gradient tube filled with ethanol/water solution using samples cut from a melt pressed (160°C) 200 μm film.

The dynamic mechanical analysis was conducted on compression-molded (160°C) test specimens. The three-point bending system of a Perkin−Elmer DMA 7 instrument was used for the measurement of storage modulus (E') and tan delta (E''/E'). The temperature scan was from −100 to +30°C at a heating rate of 4°C/min and frequency of 1 Hz. A Rheometrics System IV rheometer was used for the rheological characterization. The measurements were made at 150°C using a cone and plate fixture with a diameter of 25 mm and 2% strain.

RESULTS AND DISCUSSION

Catalyst Efficiency

In copolymerization with toluene as the medium, the $Et(Ind)_2ZrCl_2$/MAO catalyst system showed polymerization activities of ca. 20000 kg_{polym}/$mol_{Mt}*h$ (80 kg_{polym}/$g_{cat}*h$), whereas the activity of $Et(Ind)_2HfCl_2$/MAO was ca. 5000 kg_{polym}/$mol_{Mt}*h$ (20 kg_{polym}/$g_{cat}*h$). The termonomer did not affect the polymerization yield significantly.
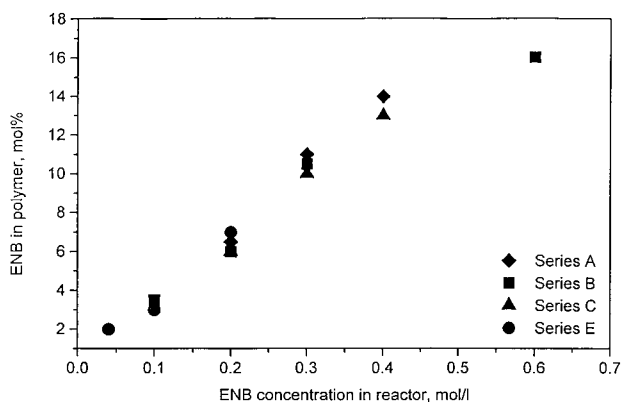
Figure 1 Ethylidene norbornene (ENB) concentration in the reactor vs. ENB content in the polymer at different ethene/propene feed ratios. Series A, B, and C: E/P feed ratios 80/20, 70/30, and 65/35 with catalyst $Et(Ind)_2ZrCl_2/MAO$. Series E: E/P feed ratio 70/30 with $Et(Ind)_2HfCl_2/MAO$ catalyst. Polymerization conditions: P 3 bar, T 40°C, 250 mL toluene, 30 min, Al/Mt 4500. The catalyst amount in polymerization was 0.5 mg of $Et(Ind)_2ZrCl_2$. $Et(Ind)_2HfCl_2$ was used in 2 mg amounts.

With the $Et(Ind)_2ZrCl_2/MAO$ catalyst, polymerization yields were significantly lower only at the largest diene concentrations. The efficiency of ethylidene norbornene incorporation is illustrated in Figure 1. Both catalyst systems incorporated ENB equally well, but there may be a slight preference for ENB at higher ethene feeds with $Et(Ind)_2ZrCl_2$. In accordance with the results of other groups,[5,8] ENB in polymerization lowered the ethene content of the polymer more than the propene content. At a higher polymerization temperature, 60°C, the yield was improved. Compared to polymerization at 40°C, more propene was incorporated, but the molar mass was reduced remarkably. In terpolymerization, both propene and diene were incorporated more effectively at 60°C. Comparing the runs with toluene and heptane as polymerization media (series B and Bh, respectively), less propene and less ENB was incorporated using heptane. Tables 1(a) and (b) list the polymerization activities and polymer composition obtained with different monomer feed ratios.

Polymer Properties: Copolymers

Characteristically, $Et(Ind)_2HfCl_2/MAO$ produces a much higher molar mass and incorporates comonomer more readily than the zirconium analogue.[14,15] In this study, the molar mass (MM) of copolymers made with $Et(Ind)_2ZrCl_2$ at 40°C was well below 100×10^3 g/mol, whereas materials produced with $Et(Ind)_2HfCl_2$ had molar mass of around 200×10^3 g/mol. Factors determining the MM were comonomer content and polymerization temperature. Polymerization at 60°C reduced the molar mass of the Hf-catalyzed copolymer to 100×10^3 g/mol. The molar mass of the $Et(Ind)_2$-$ZrCl_2$-catalyzed polymers decreased significantly with an increasing amount of comonomer. In another study by our group,[12] it was shown that an acceptably high molar mass copolymer is also produced with the Zr-based catalyst, when the polymer composition is high in ethene. At the same E/P feed ratio, the $Et(Ind)_2HfCl_2$ catalyst incorporated more propene. Comparing copolymers of similar propene content, the material produced with $Et(Ind)_2HfCl_2$ had a slightly higher density than that produced with $Et(Ind)_2ZrCl_2$. Glass transition temperatures of the copolymers were between $-59°C$ and $-55°C$. The crystallization enthalpies were below 10 J/g, and they decreased with increasing propene content in the polymer. With heptane as the polymerization medium, more ethene was incorporated than with toluene using the same E/P feed ratio. The copolymer polymerized in heptane (sample B0h) was more crystalline and had a higher density and melt flow rate than the toluene polymerized ones (samples A0 and B0) with a similar ethene content. This indicates a slightly less even monomer distribution in the chain. The melting endotherms of samples B0 and B0h are shown in Figure 2. The E/P copolymer properties are set out in Table II.

Polymer Properties: Terpolymers

The terpolymer properties are reported in Table III. Figure 2 shows DSC melting thermograms of selected experimental and commercial terpolymers. Both the melting and crystallization processes of the terpolymers were weak and extended over a large temperature range from the glass transition onwards. The commercial terpolymer samples were more crystalline than the experimental, metallocene-catalyzed terpolymers. The $Et(Ind)_2HfCl_2$-catalyzed terpolymers were amorphous when more than 2 mol % of ENB was present in the chain. The $Et(Ind)_2ZrCl_2$-catalyzed terpolymers, due to a higher ethene content, exhibited a crystallization peak still with 3 mol % ENB in the polymer. Another property that depends on both the ethene content and amount of termonomer is the glass transition temperature, T_g.

Table I   (a) Polymerizations with Et(Ind)₂ZrCl₂/MAO

E/P Gas Feed wt %	[ENB] mol/L in Reactor	E mol % in Polymer	P mol % in Polymer	ENB mol % in Polymer	Catalyst Activity kg$_{polym}$/mol$_{Mt}$*h	Sample
80/20	0	74	24	0	16800	A0
	0.2	70	23	7	17400	A2
	0.3	67	22	11	17800	A3
	0.4	64	21	15	15700	A4
75/25	0	71	29	0	16000	B0
	0	73	27	0	10800	B0h[a]
	0.1	68	29	3	16000	B1
	0.1	71	26	3	14200	B1h[a]
	0.2	66	28	6	17300	B2
	0.3	63	27	10	17700	B3
	0.6	59	25	16	11000	B6
70/30	0	65	35	0	19700	C0
	0.2	61	33	6	19800	C2
	0.3	59	31	10	16800	C3
	0.4	57	30	13	15000	C4
65/35	0	58	42	0	22500	D0
	0.1	59	38	3	22200	D1
	0.2	56	36	8	18600	D2

[a] Polymerization in heptane.
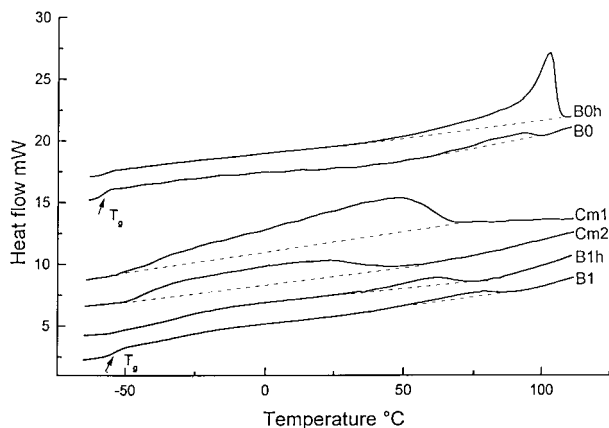
In commercial, conventional EPDMs, T_g is between −55°C and −60°C, but at high diene or low ethene content, it can be 10°–20°C higher.[1,16] The glass transition of the metallocene produced polymers was observable also with DSC, when there was less than 70 mol % ethene in the polymer. With a similar low content of ENB in the polymer, the samples containing most ethene (E) had the lowest glass transition temperatures. For example, with 3 mol % of ENB in the polymer, the Et(Ind)₂ZrCl₂-catalyzed terpolymer containing 68 mol % ethene had a T_g at −53.3°C, and the terpolymer with 59 mol % E exhibited the transition at −51.5°C. Interestingly, the Et(Ind)₂H fCl₂-catalyzed terpolymer with 58 mol % E showed a T_g at a somewhat higher temperature, −45.6°C. As the amount of diene in the polymer was in-

creased, T_g rose rapidly; with 6 mol % ENB in the polymer, T_g was observed at −39°C, with 10 mol %, at −12°C. The rise in T_g was 1.5°C per wt %, between 10 and 42 wt % of ENB in the polymer. Good agreement was found between the T_g values of the metallocene materials measured with DMA (temperature of the tan δ peak maxima) and with DSC. The DMA determined T_g values were somewhat higher than the DSC determined ones. For example, the T_g of sample E1 determined with DMA was −44.3°C, whereas DSC gave a T_g of −45.6°C. The glass transition of the polymers is further discussed with the results of dynamic mechanical analysis.

With diene in the polymer, a decrease was seen in the originally rather high GPC molar mass values of the Et(Ind)₂H fCl₂-catalyzed polymers. The Et-

Table I   (b) Polymerizations with Et(Ind)₂HfCl₂/MAO

E/P Gas Feed wt %	[ENB] mol/L in Reactor	E mol % in Polymer	P mol % in Polymer	ENB mol % in Polymer	Catalyst Activity kg$_{polym}$/mol$_{Mt}$*h	Sample
70/30	0	60	40	0	5300	E0
	0.04	59	39	2	5300	E04
	0.1	58	39	3	5500	E1
	0.2	56	37	7	4800	E2
70/30 60°C	0	59	41	0	8300	F0
	0.1	57	38	5	8200	F1

Figure 2 DSC melting endotherms of commercial, conventional E/P/ENB terpolymers (Cm1 and Cm2) and experimental, metallocene-catalyzed E/P and E/P/ENB polymers. Polymer compositions: B0h: 73 mol % E; B0: 71 mol % E, Cm1: 76 mol % E, 1 mol % ENB; Cm2: 73 mol % E, 2 mol % ENB, B1h: 71 mol % E, 3 mol % ENB, B1: 68 mol % E, 3 mol % ENB. The dotted lines are drawn to guide the eye.

$(Ind)_2ZrCl_2$-catalyzed terpolymers behaved differently in GPC analysis, showing an increasing M_w value with increasing diene feed. Probably this does not mean increased chain length, but increased rigidity of the chain resulting from the stiff ethylidene norbornene units. The same behavior was observed in the melt flow rates of the polymers. With increasing ENB content, the MFR values of the $Et(Ind)_2$-$ZrCl_2$-catalyzed materials decreased, whereas the MFR values of the $Et(Ind)_2HfCl_2$-catalyzed materials increased. Incorporation of the bulky ring structure into the chain also resulted in material having a greater density. The increase was more rapid with polymers containing more ethene. The molar mass distribution curves were narrow, with no shouldering present. Also, the solubility supports the assumption that the polymers were not crosslinked. All the experimental polymers were soluble in toluene at ambient temperature. The shape of the molar mass distribution curves of the metallocene-catalyzed terpolymers and conventional, vanadium-catalyzed EPDM terpolymer is compared in Figure 3. The commercial EPDM had a tail in the molar mass distribution curve, which was not seen in the metallocene-catalyzed materials. The molar mass distribution of the metallocene polymers became slightly narrower with increasing content of the termonomer, a phenomenon that has also been observed in other metallocene-catalyzed terpolymerizations by our group.[17]

Table II   Properties of the E/P Copolymers

Catalyst	E mol % in Polymer	E wt % in Polymer	M_w 10^{-3} g/mol	MMD	T_g (DSC) °C	T_g (DMA)[a] °C	T_{cryst} °C	Delta H_{cryst} J/g	MFR 125°C g/10 min	MFR 190°C g/10 min	Density g/cm³	Sample
1	74	65	62	2.1	n.d.		76.3	9.8	1.3/2.16 kg		873	A0
1	71	62	57	2.1	−59.4	−55.2	57.0	8.2	1.7/2.16 kg		867	B0
1	73	64	67	2.2	n.d.	−58.8	76.1	19.3	2.9/5.00 kg		879	B0h[b]
1	65	55	50	2.2	−59.4	−55.4	48.4	6.2	3.9/2.16 kg		863	C0
1	58	48	45	2.0	−58.5		38.9	2.0	4.5/2.16 kg		878	D0
2	60	52	220	2.6	−55.7		49.7	2.4		0.4/5.00 kg	889	E0
2	58	48	100	2.4	−55.6	−55.1	51.6	0.7	0.3/2.16 kg	1.7/2.16 kg	891	F0[c]

[a] tan delta peak temperature.
[b] Polymerization in heptane.
[c] Polymerization at 60°C.
n.d. not detected.
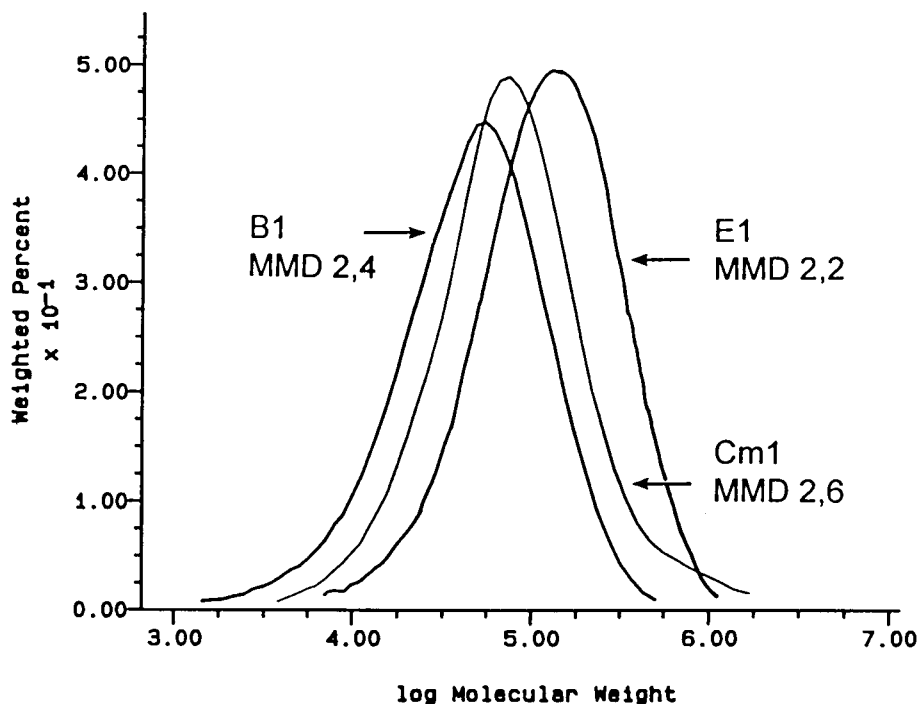Catalyst 1 = $Et(Ind)_2ZrCl_2$/MAO, 2 = $Et(Ind)_2HfCl_2$/MAO.

Table III   Properties of the E/P/ENB Terpolymers

Catal.	E mol % in Polymer	E wt %	P mol % in Polymer	ENB mol % in Polymer	ENB wt %	M_w 10^{-3} g/mol	MMD	T_g (DSC) °C	T_g (DMA)[a] °C	MFR/125°C g/10 min	Density g/cm³	Sample
1	68	55	29	3	10	62	2.4	−53.3	−55.4	0.9/2.16 kg	868	B1
1	71	58	26	3	10	73	2.2	n.d.	−54.6	0.9/5.00 kg	882	B1h[b]
1	59	46	38	3	10	51	1.9	−51.5		4.2/2.16 kg	888	D1
2	59	47	39	2	7	220	2.3	−50.6	−44.8	0.1/5.00 kg	874	E04
2	58	45	39	3	10	157	2.2	−45.6	−44.3	0.1/5.00 kg	882	E1
2	57	42	38	5	16	72	2.0	−45.6		1.6/5.00 kg	890	F1[c]
1	70	52	23	7	22	73	2.0	−25.6		0.4/2.16 kg	902	A2
1	66	49	28	6	19	66	2.0	−38.5		0.9/2.16 kg	919	B2
1	61	45	33	6	19	58	2.1	−39.4		1.5/2.16 kg	894	C2
1	56	39	36	8	24	61	2.0	−33.6		1.3/2.16 kg	902	D2
2	56	40	37	7	21	166	2.1	−32.8	−30.8	0.2/5.00 kg	905	E2
1	67	45	22	11	32	89	2.1	−9.7		0.15/2.16 kg	926	A3
1	63	43	27	10	29	79	2.0	−11.9		0.3/2.16 kg	935	B3
1	59	40	31	10	29	73	2.1	−11.1		0.4/2.16 kg	927	C3
1	64	40	21	15	40	103	1.9	2.5			921	A4
1	57	36	30	13	35	75	1.8	−2.3		0.3/2.16 kg	931	C4
1	59	36	25	16	42	102	1.8	16.7			955	B6
Ref. 1	76	66	23	1	4	112	2.6	n.d.	−36.8	0.2/5.00 kg	882	Cm1
Ref. 2	73	61	25	2	7	214	2.9	n.d.	−36.3	0.1/5.00 kg[d]	860	Cm2

[a] tan delta peak temperature.
[b] Polymerization in heptane.
[c] Polymerization at 60°C.
[d] Measured at 190°C.
n.d. not detected.
Catalyst 1 = Et(Ind)$_2$ZrCl$_2$/MAO, 2 = Et(Ind)$_2$HfCl$_2$/MAO.

Figure 3 The molar mass distribution curves for conventional E/P/ENB (sample Cm1) and experimental terpolymers produced with metallocene catalysts Et(Ind)$_2$-ZrCl$_2$/MAO and Et(Ind)$_2$H f Cl$_2$/MAO (samples B1 and E1, respectively).

Viscoelastic Properties

The dynamic viscoelastic properties of the un-cured samples were studied with DMA and with a small-amplitude oscillating rheometer. The DMA measurement temperature range was from $-100°C$ to around $+30°C$, where the samples began to soften or flow. The small-amplitude oscillating rheology measurements were done at 150°C. The storage modulus E', as determined by DMA, is related to material stiffness.[18] Above T_g, the storage modulus varies with material crystallinity, the materials containing some degree of crystallinity are stiffer and, therefore, able to carry the load up to higher temperatures.[1,16] Figure 4 shows the dependence of elastic storage modulus E' on temperature for the experimental metallocene and commercial terpolymers. E/P copolymers were included for comparison. The effect of comonomer content was clearly seen in the behavior of the metallocene E/P copolymers, B0h and F0. Above T_g, the partly crystalline copolymer B0h (73 mol % ethene) retained considerable stiffness at higher temperatures compared with the amorphous copolymer, F0 (58 mol % ethene). Below T_g, the metallocene terpolymer E1, with 58 mol % of E and 3 mol % of ENB had the highest

storage modulus. In contrast to the corresponding E/P copolymer, the amorphous terpolymer retained some ability to carry load up to ambient temperature. The most crystalline terpolymer,
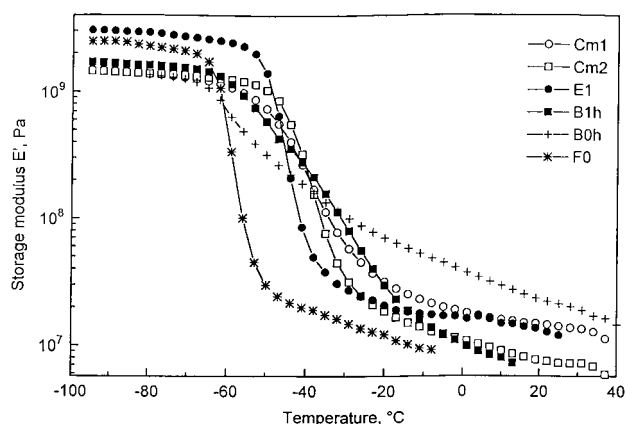
Figure 4 Storage modulus E' of the polymers as a function of temperature. Samples Cm1 and Cm2 were commercial, conventional E/P/ENB terpolymers, E1, and B1h metallocene-catalyzed terpolymers, B0h and F0 were E/P copolymers produced with the metallocene catalysts.
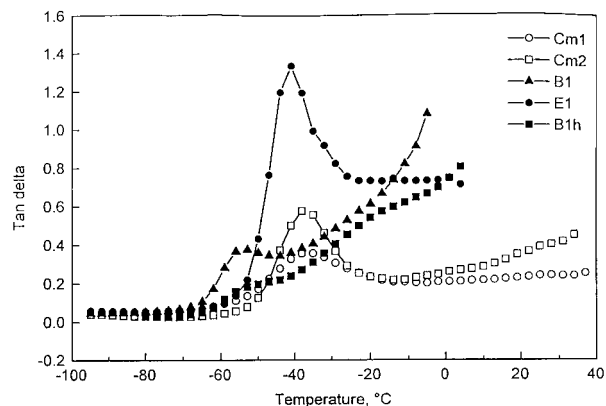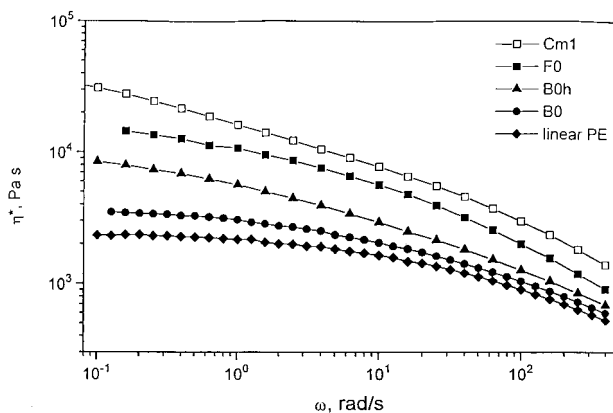
Figure 5 Tan δ of the polymers as a function of temperature. Samples Cm1 and Cm2 were commercial, conventional E/P/ENB terpolymers, E1, B1, and B1h metallocene-catalyzed terpolymers.

Figure 6 Copolymer dynamic viscosity against angular frequency at 150°C. For comparison, a terpolymer (Cm1), and a linear (HD) PE were inserted. The molar mass of the HDPE was 72 000 g/mol with MMD of 4.3.

Cm1, was the stiffest of the terpolymers above T_g, but the experimental metallocene terpolymers were closely behind. It has to be borne in mind, however, that these are not crosslinked materials. Obviously, crosslinks are needed to improve mechanical strength.

The damping factor, tan δ, is the ratio of the dynamic loss (viscous) modulus E'' to the dynamic storage (elastic) modulus E'. It gives information about the relative contributions of the viscous and elastic components of a viscoelastic material. The tan δ peak maxima at the glass– rubber transition is often defined as the T_g. Differences in comonomer amounts and distribution in copolymers are reflected in the location and intensity of the tan δ peak at the glass–rubber transition.[17–20] A high-intensity of the peak at the β-transition corresponds to a more amorphous material.[19,20] High intensity of the damping curve may also indicate higher impact strength of the material at temperatures below zero.[21] The tan δ curves of the terpolymers are represented in Figure 5. Interestingly, the samples B1 and B1h displayed a weaker and earlier glass transition than the reference materials Cm1 and Cm2, although their lower molar ethene contents. The sample with the highest propene content, E1, produced the most intense tan δ peak at a temperature close to that of the commercial materials.

Melt rheology provides insight into the relationships between viscoelasticity, molecular structure, and processing performance. The limiting, rate-independent viscosity at low deformation rates is designated the zero shear viscosity η_0, and is strongly dependent on the molar mass. The dependence of

viscosity on the rate of deforming, the shear sensitivity, gives information about ease of processing. Flexible polymers have lower viscosities than rigid polymers of a similar molar mass, and furthermore, any factor that increases the T_g tends to increase the viscosity.[22] For EPDM, η_0 is often too high to be measured.[1] Figure 6 presents the copolymer and Figure 7 the terpolymer melt viscosity curves from dynamic rheological measurements. The viscosity of all but the lowest molar mass samples was clearly rate dependent, even at the lowest rates. A non-metallocene, high-density polyethene is inserted in Figure 6 for comparison. The shear thinning behavior of the copolymers resembled that of conventional HDPE. The terpolymers exhibited greater shear sensitivity. The chain stiffening effect of the bulky ENB groups in the polymer chain could explain the
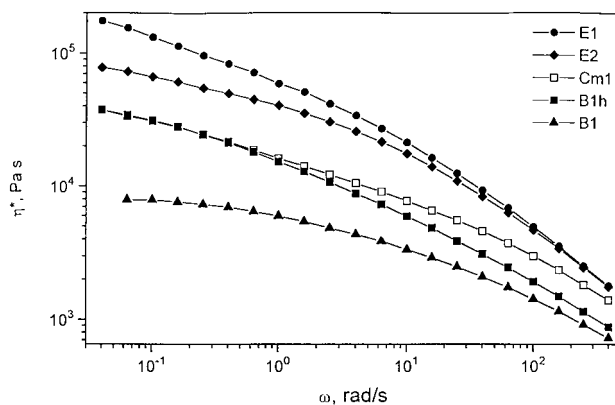
Figure 7 Terpolymer dynamic viscosity against angular frequency at 150°C.
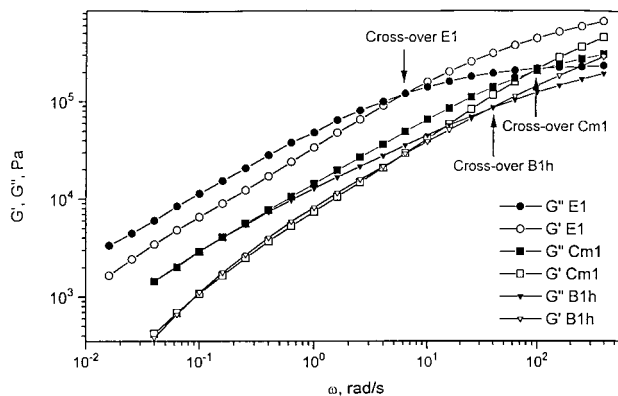
Figure 8 Dynamic storage and loss modulus of selected terpolymers as a function of angular frequency at 150°C.

much higher viscosity of the terpolymer samples in comparison with the corresponding copolymers. Increased viscosity due to crosslinking or branching does not seem likely, as the 6 mol % ENB terpolymers did not show higher viscosity than the terpolymers with 3 mol % of ENB (see samples E2 and E1 in Fig. 7). In Figure 8, the storage and loss moduli are plotted against angular frequency. An increase in molar mass results in a decrease in the crossover frequency of the moduli,[23] clearly seen when comparing samples B1h and E1. Samples B1h and Cm1, although of different molar mass and different ENB content, showed quite similar behavior at low frequencies.

CONCLUSIONS

$Et(Ind)_2ZrCl_2/MAO$ and $Et(Ind)_2HfCl_2/MAO$ catalysts were utilized for ethene/propene and ethene/propene/5-ethylidene-2-norbornene terpolymerization. The $Et(Ind)_2ZrCl_2$ catalyst was found to be useful when E/P copolymers rich in ethene are produced, whereas the $Et(Ind)_2HfCl_2$ catalyst is beneficial when high amounts of propene in the copolymer are desired. The activity of the $Et(Ind)_2ZrCl_2$ catalyst was several times the activity of the Hf analogue. In E/P/ENB terpolymerization, the minor decrease in polymerization activity with increasing termonomer concentration, together with the ease of diene incorporation in the chain were noteworthy. By varying the monomer feed ratios and the polymerization media, materials with widely differing compositions can be produced. On the basis of the steady change in polymer properties such as

crystallinity, T_g and density with increasing co- and termonomer content it seems likely that the monomers were evenly distributed along the chain. The thermal and viscoelastic behavior of the uncrosslinked metallocene polymers was studied in comparison with conventional EPDMs. At similar molar monomer contents, the metallocene-catalyzed polymers were less crystalline and had lower glass transition temperatures. At temperatures below T_g, the metallocene materials were stiffer. In the melt, in addition to molar mass, the amount of termonomer affected the viscosity.

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