# Influence of the Polymerization Conditions on the Rigidity of Phenylnorbornene–Ethylene Copolymers Made Using Ethylene bis (indenyl) zirconium dichloride and MAO

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**ABSTRACT:** When characterized with DMA it was found that Phenylnorbornene-ethylene copolymers with equivalent comonomer concentrations had very different storage moduli in the glassy state as well as glass transition temperatures. NMR analysis of the copolymers revealed that they had different ratios of Exo- and Endo-diastereomers even if the same comonomer composition had been used. The Exo/Endo-ratio in the polymer was surprisingly higher than in the monomer and increased with higher incorporations of the comonomer. Copolymers with higher Exo/Endo-ratios also had a tendency for lower storage moduli in the glassy state and higher tan  $\delta$  peaks. These properties are valuable because more flexible and impact-resistant copolymers are obtained. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 385–393, 1998

**Key words:** cyclic olefin copolymer; phenylnorbornene; metallocene catalyst; NMR; DMA

#### INTRODUCTION

Norbornene–ethylene copolymers are manufactured in the semicommercial scale using metallocene catalysts and methylaluminoxane (MAO) as a cocatalyst.<sup>1</sup> Amorphous and heat-resistant cyclo–olefin copolymers (COC) are marketed by Hoechst<sup>2</sup> (TO-PAS) and Mitsui Sekka<sup>3</sup> (APEL) mainly for optical applications like compact discs. Idemitsu Kosan,<sup>4</sup> on the other hand, manufactures norbornene-ethylene copolymers with lower norbornene concentrations to obtain lower glass transition temperatures ( $T_g$ ), and hence, elastomeric properties. Such low  $T_g$  COCs will be used for the replacement of plasticized PVC in cling films.

One very serious problem with the norbornene-ethylene copolymers is that they are very brittle below their glass transition temperatures.<sup>5</sup> The engineering type COCs are very brittle at room temperature and the elastomeric type COCs become brittle at deep freezing temperatures.

To overcome the deficiencies caused by norbornene it is suggested that phenylnorbornene is used instead, either alone or in combination with norbornene.

The intention with this publication is to get information about the rigidity of phenylnorbornene-ethylene copolymers below their glass transition temperatures and how it is affected by the polymerization conditions. For this purpose DMA measurements were made and the influence of the polymerization conditions on the storage modulus and tan  $\delta$  was studied.

# **EXPERIMENTAL SECTION**

# **Apparatus and Polymerization Method**

The polymerization of phenylnorbornene and ethylene was done using a semiflow method and a

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reactor system described in detail in an earlier article of our group.<sup>6</sup> The appropriate amount of phenylnorbornene was dissolved in toluene and diluted so that a 200-mL solution was obtained. The solution was dried with molecular sieves overnight and poured into a thermostated 500 mL stainless steel reactor equipped with a stirrer. After purging with nitrogen and ethylene the ethylene pressure and the temperature of the reactor content were set at the chosen values and ethylene was supplied until the toluene solution was saturated and the ethylene flow stopped. Then the MAO-toluene solution was pumped into the reactor and the mixing continued for 15 min. Finally, the catalyst-toluene solution was pumped to the reactor. After addition of catalyst (2 mg  $= 24 \cdot 10^{-6} \text{ mol/L or } 1 \text{ mg} = 12 \cdot 10^{-6} \text{ mol/L of}$ ethylene bis (indenyl) zirconium dichloride) the polymerization was allowed to continue for 30 min or 60 min, and the ethylene consumed in the polymerization was constantly replaced and the pressure and temperature were automatically controlled. No hydrogen or other chain transfer agents were used in this study. When the chosen polymerization time was finished, the ethylene supply was shut, the reactor vented, and the reactor content poured into ethanol (300 mL). Then hydrochloric acid was added in order to deactivate MAO and the sample was kept that way until the next day when it was filtered, washed with acetone, filtered again, and dried in a vacuum oven.

#### Chemicals

The comonomer, 5-phenyl-2-norbornene (5-phenyl-bicyclo-(2,2,1)-hept-2-ene), was synthesized from cyclopentadiene and styrene through a Diels-Alder-reaction. 120 g (1 eq.) cyclopentadiene obtained by distilling dicyclopentadiene, 250 mL (1.2 eq.) styrene, and 33 g (0.08 eq.) N-Phenyl-2-naphtylamine (inhibitor for polymerization of styrene) were dissolved in toluene and the solution (500 mL) was poured into a 1-liter thermostated steel reactor that was evacuated and purged with nitrogen. Under mixing and controlling the temperature at 195°C the reaction was allowed to continue for 21 h, after which it was distilled under vacuum. The purified phenylnorbornene was analyzed with <sup>1</sup>H-NMR as described below, and the diastereomer ratio obtained was 27% Exo/73% Endo.

Also, norbornene (bicyclo-(2,2,1)-hept-2-ene)

was used in some reference polymerizations, and this was obtained from Fluka (14351) and had a purity of 97%. The ethylene used was AGAs grade 2.7, which was further purified in columns containing molecular sieves, CuO, and  $Al_2O_3$  before entering the reactor, and the toluene used was Riedel-deHäen's grade RG.

The catalyst was the soluble metallocene catalyst ethylene bis (indenyl) zirconium dichloride, "EURECEN 5036," from Witco and the cocatalyst was 10 wt % methylaluminoxane (MAO) in toluene from Witco. The Al content of the cocatalyst was 4.5-5.5 wt %.

#### **Polymer Characterization**

The phenylnorbornene concentrations in the copolymers as well as the diastereomer ratios in the copolymers and the comonomer were measured by <sup>1</sup>H-NMR. The spectra were recorded at 100°C with 1,1,2,2-tetrachloroethane as solvent. A spectral width of 15,000 Hz, an acquisition time of 1.0 s with 32768 data points and a 20° pulse were used to accumulate 32 scans. In Figure 1 is presented the spectra of a phenylnorbornene–ethylene copolymer and the phenylnorbornene concentration can be calculated according to eq. (1) seen below.

Phenylnorbornene (mol %)

$$=\frac{\frac{1}{5}A_{1}}{\frac{1}{4}(A_{2}-\frac{9}{5}A_{1})+\frac{1}{5}A_{1}}\cdot 100 \quad (1)$$

 $A_1$  is the integrated area of the aromatic hydrogens (6.4–7.8 ppm) and  $A_2$  is the area of all other hydrogens (0–4 ppm).  $A_2$  contains the aliphatic hydrogens of ethylene (4) as well as phenylnorbornene (9), which need to be substracted from  $A_2$ to obtain the integral of the ethylene units.

The Exo/Endo-ratio can be obtained from the integrals at 2.7 ppm (Exo) and 3.2 ppm (Endo), which represent the aliphatic hydrogens in geminal position to the phenyl group. These assignments have been confirmed by <sup>1</sup>H-<sup>1</sup>H-cosy. Also, the enchainment of phenylnorbornene was exclusively in the Exo-configuration, which was confirmed by this same <sup>1</sup>H-<sup>1</sup>H-cosy. Exclusive enchainment of norbornene in the Exo-configuration has earlier been shown by Kaminsky et al.<sup>7</sup> However, according to molecular modelling, the other



**Figure 1** <sup>1</sup>H-NMR spectrum for a phenylnorbornene–ethylene copolymer made with a metallocene catlyst and MAO.

two enchainment possibilities, Endo and Exo, Endo, would provide stiffer polymer chains with higher  $T_g$ , but there has not been any experimental evidence yet.

For evaluating the rigidity of the copolymers in the glassy state, their glass transition temperatures as well as their potentials for high-impact properties DMA measurements were made. For this purpose compression-molded plaques of the size  $2 \times 4 \times 15$  mm were made and the measurements were performed using the Perkin-Elmer instrument DMA 7 interfaced to a DEC station 325C and equipped with a Unox software. The mechanical mode used was the three-point bending system and the analyses were run in a temperature scan mode. The heating rate was 4°C/min, the frequency 1 Hz, and the temperature behavior was characterized by monitoring the changes in strain and phase. The dynamic storage modulus (E'), dynamic loss modulus (E''), and damping  $(\tan \delta = E''/E')$  were monitored, and in Figure 2 the curves obtained for run 7 are presented.

The dynamic storage modulus or elastic modulus, E', is an indication of how the material can store mechanical energy. E' is approximately similar to the Young or elastic modulus, or stiffness.<sup>8</sup> Thus, the E' onset defines the temperature at which the material's strength will begin to decrease, such that the material may no longer be able to bear a load without deforming. Nunnery has recently explained that storage modulus indeed agrees closely with flexural modulus as measured by ASTM D790.<sup>9</sup>

The dynamic loss modulus or viscous modulus, E'', is a measure of the energy absorbed due to a relaxation and, thus, is useful in clarifying the mechanism of internal motions. It is a measure of the dissipated heat during a deformation, and



**Figure 2** DMA-scan for a phenylnorbornene–ethylene copolymer made with a metallocene catalyst and MAO (run 7). E' = storage modulus, E'' = loss modulus, tan  $\delta$  = E''/E'.

the peak in loss modulus represents the temperature at which a material is undergoing the maximum change in polymer mobility, which corresponds to one definition of the glass transition temperature,  $T_g$ .

The damping or dissipation factor,  $\tan \delta$ , is the ratio of E'' to E', and gives information on the relative contributions of the viscous and elastic components of a viscoelastic material. Materials with a tan  $\delta$  value less than 1 exhibit more elastic behavior, and materials with a tan  $\delta$  value above 1 more viscous behavior. Tan  $\delta$  also shows a maximum and most of the DMA reference data refer to this maximum as  $T_g$ .

As a measure for the rigidity in the glassy state E' at  $-25^{\circ}$ C was arbitrarily chosen because at this temperature the onset of softening had not yet taken place for any of the copolymers studied. The temperature of the tan  $\delta$  peak was taken as a measure for the glass transition temperature  $(T_g)$  and the height of the tan  $\delta$  peak (max value – base line value) was calculated because it has been shown that it correlates with the impact properties of polymers with equivalent  $T_g$ s.

The DMA technique has also been mentioned in the litterature for prediction of the impact tran-

sitions of polymers. Heijboer proposed already in 1968 a qualitative correlation between the mechanical damping peaks and impact toughness of polymers.<sup>10</sup> Turley and Keskkula obtained good agreement between the integrated area against temperature of rubber damping peaks represented by tan  $\delta$  at subambient temperatures and Izod impact at ambient temperatures for a series of butadiene modified polystyrenes.<sup>11</sup> Recently, Woo successively used DMA measurements to study the low-temperature impact properties of metallocene catalyzed polyethylenes and their blends with polypropylene homopolymers as well as studies of flexible polyvinylchloride (PVC), ethylene vinyl acetate (EVA), and polypropylene films between about  $-100^{\circ}$ C and  $+60^{\circ}$ C.<sup>12,13</sup> These studies of DMA analysis and its relationship to impact transitions also prompted us to make some corresponding comparisons for the studied cyclic copolymers.

In Figure 3 are presented the E' and tan  $\delta$  scans of a stiff (run 7) and a soft (run 1) phenylnorbornene-ethylene copolymer with equivalent  $T_g$ s in comparison with a norbornene-ethylene copolymer with higher  $T_g$  (run 11). It can be seen that the E' at  $-25^{\circ}$ C is higher for the norborne-



**Figure 3** DMA-scans for a soft (-) and a stiff (-) phenylnorbornene-ethylene copolymer with equivalent  $T_g$ s in comparison with a norbornene-ethylene copolymer (---) with higher  $T_g$ .

ethylene copolymer compared to the phenylnorbornene-ethylene copolymers.

A very convenient way of measuring  $T_g$  is the DSC method. This technique, however, measures glass transitions, which are sometimes very difficult to distinguish. In Figure 4 is presented the DSC curve for run 7 obtained with the Mettler-Toledo TA8000DSC so that the sample was first heated to 200°C, then cooled to  $-20^{\circ}$ C ( $20^{\circ}$ C/min)) and reheated to  $140^{\circ}$ C ( $20^{\circ}$ C/min)). The data was taken from the second heating and the glass transition started at  $12^{\circ}$ C with a midpoint temperature of  $19^{\circ}$ C. This should be compared with the tan  $\delta$  max midpoint temperature of  $18^{\circ}$ C obtained from the DMA curve in Figure 2. No crystalline melting point was seen for run 7 nor any other co- or ter-polymer included in this study.

#### **RESULTS AND DISCUSSION**

# Influence of the Amount of Phenylnorbornene and Al/Zr Ratio

Three levels of phenylnorbornene, 7, 10, and 15 g, were polymerized at  $30^{\circ}$ C for 30 min main-

taining an ethylene pressure of 4 ata and the Al/ Zr ratio 3000. For 10 g phenylnorbornene also three levels of Al/Zr ratio, 1500, 3000, and 6000, were compared. The results of these polymerizations can be seen in Table I.

It can be seen from the results in Table I that under all conditions the Exo-diastereomer of phenylnorbornene was more easily incorporated into the copolymer chain than the Endo-diastereomer. The portion of Exo increased from 27% up to 49% in the polymerization. This is contrary to the results obtained by Kaminsky et al. using other catalysts.<sup>14</sup> The activities were very similar and the incorporations of phenylnorbornene as well as the  $T_{gs}$  (tan  $\delta$  max) were not very much influenced by the amount of comonomer added nor the Al/ Zr ratio. The stiffnesses below  $T_g$ , E' (-25°C), however, increased with increasing incorporations of phenylnorbornene. Also the Exo-contents and the heights of tan  $\delta$  max increased slightly for 3000 Al/Zr. The influence of Al/Zr ratio was most strongly seen in the Exo-concentrations. When decreasing the Al/Zr ratio the Exo-concentration increased, the height of tan  $\delta$  max increased, and the stiffness below  $T_g$  decreased.



**Figure 4** DSC scan for a phenylnorbornene–ethylene copolymer made with a metallocene catalyst and MAO (run 7).

Molecular modelling shows that the distance between the copolymer chains is longer for the Exodiastereomer than the Endo-diastereomer of phenylnorbornene, which would create a less compact copolymer with increased mobility (decreasing effect on  $T_g$ ) and a lower stiffness. However, the Exo-diastereomer also rotates more slowly around the polymer chain and makes a single chain stiffer (increasing effect on  $T_g$ ). A net effect of Exo-concentration on  $T_g$  is, therefore, very difficult to see.

## Influence of Ethylene Pressure, Polymerization Time, Temperature, and Catalyst Concentration

Three levels of ethylene pressure, 2, 3, and 4 ata, were used when copolymerizing 10 g of phenyl-

mol/L Ethylene Bis (Indenyl) Zirconium Dichloride and MAO in Toluene
Phenylnorbornene–Ethylene Copolymers Polymerized for 30 min at 30°C and 4 ata using 24 $ imes$ 10 <sup>-6</sup>
Table 1 Influence of Phenylnorbornene Content and AL/Zr Ratio on the Properties of

	PhN (g)	hN (g) AL/Zr		Activity	1		DMA		
Run					<sup>1</sup> H-N	IMR	Tan $\delta$ max		
			Yield (g)	(10 <sup>6</sup> g/mol Zr h ata)	PhN Conc. (mol %)	Exo Conc. (%)	(°C)	(height)	<i>E'</i> (-25°C) (10 <sup>9</sup> Pa)
1	7	3000	12.4	1.3	11	44	20	0.80	0.67
<b>2</b>	10	3000	12.3	1.3	12	46	21	1.12	1.09
3	15	3000	13.9	1.4	15	47	23	1.27	1.20
4	10	1500	12.5	1.3	13	49	22	1.22	0.86
<b>5</b>	10	6000	13.4	1.4	12	44	16	1.13	1.04

									DMA			
						Activity	<sup>1</sup> H-N	IMR	Ta	n $\delta$ max	<i>E'</i> (-25°C) (10 <sup>9</sup> Pa)	
Run	P (ata)	t (min)	T (°C)	Cat. (mg)	Yield (g)	(10 <sup>6</sup> g/mol Zr h ata)	PhN Conc. (mol %)	Exo Conc. (%)	(°C)	(Height)		
6	2	30	30	2	10.8	2.3	17	48	35	1.50	1.09	
7	3	30	30	<b>2</b>	14.5	2.0	11	42	18	0.85	1.53	
<b>2</b>	4	30	30	<b>2</b>	12.3	1.3	12	46	21	1.12	1.09	
8	3	60	30	<b>2</b>	14.0	1.9	8	40	21	0.66	1.44	
9	3	30	50	2	14.8	2.1	16	43	31	1.13	1.38	
10	3	30	30	1	7.7	2.1	12	44	21	1.02	0.85	

Table IIInfluence of Ethylene Pressure, Polymerization Time, Temperature, and CatalystConcentration on the Properties of Phenylnorbornene-Ethylene Copolymers Polymerized UsingEthylene Bis (Indenyl) Zirconium Dichloride, 3000 Al/Zr of MAO and 10 g of Phenylnorbornene

norbornene at 30°C and 3000 Al/Zr for 30 min. At 3 at a also the influence of polymerization time (60 min), temperature (50°C), and amount of catalyst (1 mg) were investigated. The results of these polymerizations can be seen in Table II.

It can be seen from the results in Table II that the activity decreased slightly when increasing the ethylene pressure. Also the incorporation of phenylnorbornene decreased due to the higher ethylene concentrations, and this was also causing lower  $T_g$ s. The lowest Exo-content was obtained for 3 ata, which is also seen in the high stiffness below  $T_g$  and the low height of tan  $\delta$  max. When polymerizing at 3 ata for 60 min the Exocontent as well as the height of tan  $\delta$  max were even lower. Also, in this case the stiffness below  $T_g$  was high in spite of the low incorporation of phenylnorbornene.

When increasing the polymerization temperature to 50°C, the incorporation of phenylnorbornene as well as  $T_g$  increased. The Exo-concentration increased slightly, the stiffness below  $T_g$  decreased, and the height of tan  $\delta$  max increased.

When using a lower catalyst concentration the yield was, of course, lower, but the activity, the incorporation of phenylnorbornene, and  $T_g$  were about the same. The Exo-concentration was, however, higher, which is also seen in a lower stiffness below  $T_g$  and a higher tan  $\delta$  max. One can imagine that with a lower catalyst concentration there is more monomer (Ethylene, Exo-phenylnorbornene, and Endo-phenylnorbornene) available for each active site so the incorporation of the more reactive Exo-diastereomer becomes more stressed.

The reason for the higher Exo-concentrations obtained at 4 ata (all runs in Table I) might also be due to the higher availability of monomers for each active site facilitating the incorporation of the more reactive monomers (Ethylene and Exophenylnorbornene).

In Figure 5 are presented the heights of tan  $\delta$  max vs. Exo-concentrations for all phenylnorbornene-ethylene copolymers presented in Tables I and II. It can be seen that there is a correlation between these fundamental properties in spite of the very different polymerization conditions.

## Influence of the Incorporation of Small Amounts of Phenylnorbornene into a Norbornene-Ethylene Copolymer

In this work it was found that by incorporating phenylnorbornene into an ethylene copolymer chain different DMA curves were obtained for dif-



**Figure 5** Heights of tan  $\delta$  max versus exo-concentrations for all phenylnorbornene–ethylene copolymers presented in Tables I and II.

			Yield (g)	Activity (10 <sup>6</sup> g/mol Zr h ata)		DMA		
Run	Norb. (g)	Phen. Norb. (g)			Ta (°C)	n δmax (Height)	<i>E'</i> (-25°C) (10 <sup>9</sup> Pa)	Charpy Impac Unnotched (kJ/m <sup>2</sup> )
11 12 13	$68.5 \\ 68.5 \\ 68.5$	6.2 12.4	$9.9 \\ 4.6 \\ 1.4$	$1.1 \\ 0.5 \\ 0.2$	$153 \\ 154 \\ 156$	0.89 1.13 1.29	2.1 2.4 2.5	$3.7 \\ 5.5 \\ 6.4$

 
 Table III
 Influence of the Incorporation of Small Amounts of Phenylnorbornene into a Norbornene-Ethylene Copolymer

ferent degrees of incorporation and different polymerization conditions. For a certain degree of incorporation and level of  $T_g$  it is advantageous to have a lower stiffness below  $T_g$  and higher tan  $\delta$  max to obtain a more flexible and impact resistant product. Because DMA seemed to be a very practical tool for the characterization of these properties we wanted to use it also for studying the influence of the incorporation of small amounts of phenylnorbornene into a norbornene–ethylene copolymer. For this purpose the properties of three polymers presented in Table III were compared. Run 11 was done by using a 200-mL toluene solution containing 68.5 g norbornene (90 mol %) and poly-

merizing it at 50°C and 4 ata for 30 min. The amount of catalyst was 2 mg and the Al/Zr ratio was 1000. Runs 12 and 13 were done in the same way but with 6.2 g and 12.4 g of phenylnorbornene in addition to 68.5 g of norbornene (the norbornene/phenylnorbornene molar ratios were 20/1 and 10/1, respectively).

It can be seen from the results in Table III that the yield and activity decreased when adding phenylnorbornene to the norbornene-toluene solution. This result is, however, dependent on the catalyst system and the polymerization conditions and is, therefore, not important in this context. From the DMA curves it can be seen that when



Figure 6 DMA scan for a norbornene-phenylnorbornene-ethylene ter-polymer (run 12).

the total amount of cyclic comonomer was increased,  $T_g$  and the stiffness below  $T_g$  also increased. It can also be seen that the height of tan  $\delta$  max increased reflecting an increase in the impact resistance measured by the unnotched Charpy method. The stiffness at  $-25^{\circ}$ C was significantly higher for these norbornene-rich co-/ ter-polymers compared to the copolymers containing no norbornene and presented in Tables I and II. However, for both runs 12 and 13 the storage modulus, E', decreased more rapidly after  $-25^{\circ}$ C, indicating an increasing mobility of the phenyl group in phenylnorbornene. This was not seen in run 11. One can say that the norbornenephenylnorbornene-ethylene ter-polymers have two transition temperatures, one representing the mobility of the phenyl group and another representing the mobility of the main chain. These two transitions can be seen in Figure 6, where the DMA curve of run 12 is presented.

# **CONCLUSIONS**

When copolymerizing phenylnorbornene and ethylene using the metallocene catalyst ethylene bis (indenyl) zirconium dichloride and MAO the Exo/ Endo ratio of phenylnorbornene was higher in the copolymer than in the monomer. It was also found that higher Exo/Endo ratios were obtained for higher ethylene pressures and lower Al/Zr ratios, leading to higher tan  $\delta$  max peaks in DMA measurements. Higher incorporations of phenylnorbornene increased  $T_g$  as well as the stiffness below  $T_{\sigma}$  for phenylnorbornene–ethylene copolymers as well as norbornene-phenylnorbornene-ethylene ter-polymers. The stiffnesses below  $T_g$  were, however, much lower for the phenylnorbornene-ethylene copolymers than for the norbornene co-/terpolymers indicating higher flexibility. Higher tan  $\delta$  max peaks were also obtained when incorporating small amounts of phenylnorbornene into a norbornene–ethylene copolymer, and this change in basic properties was also seen in higher Charpy Impact results. Further improvement in Charpy Impact can be expected when using phenylnorbornene with higher Exo/Endo ratio and polymerization conditions that further increase the Exo/ Endo ratio. The metallocene catalyzed norbornene–ethylene copolymers that are now on the market are too brittle for many applications, and by incorporating small amounts of phenylnorbornene into them this drawback can be eliminated.

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