Thermal and Dynamic Mechanical Behavior of Ethylene/Norbornene Copolymers with Medium Norbornene Contents

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ABSTRACT: A range of ethylene/norbornene copolymers were synthesized using the commercially available rac-Et(Ind)$_2$ZrCl$_2$ metallocene catalyst. A large window of norbornene contents, between 30 and 55 mol % was used to facilitate the interpretation of the results. The polymers were characterized by means of wide-angle X-ray scattering, differential scanning calorimetry, and dynamic mechanical thermal analysis. The X-ray diffractograms showed two amorphous halos, the low-angle one increasing in the intensity with norbornene content. Calorimetric and dynamic mechanical results led to a linear relation between the glass transition temperature and the norbornene content. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2159–2165, 2001

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INTRODUCTION

Recent progress in metallocene catalysis has led to the development of a wide range of polyolefin materials. The most interesting observation is that the architecture of the polymer can be tailored to meet its end-use by employing a specific catalyst. Presently a large number of groups have been concentrating on the synthesis of cycloolefin copolymers (COCs).[1–10] That is, ring structures, such as norbornene, are copolymerized with ethylene to obtain a new class of amorphous polymers. It is possible to obtain these COCs on a semicommercial basis from either Ticona or Mitsui Chemicals. The COCs available in Europe from TICONA go under the tradename "TOPAS" (Thermoplastic Olefin Polymers of Amorphous Structures). Cycloolefin copolymers are characterized by their excellent transparency, high stability against hydrolysis and chemical degradation, and processability. These properties make them interesting materials for use in optical applications and compact disks among others.

The complexity of these polymers is reiterated by the wide variety of different behaviors already found in literature. In general, the polymers are amorphous; however, both Arndt et al.[4] and Harrington et al.[8] have observed crystallinity in polymers having low or high norbornene incorporations. The presence of a degree of stereoregularity in the distribution of monomer units was attributed as being the influencing factor. The speed and simplicity of the DSC measurements makes this technique the ideal method to measure the thermal behavior of these COCs. Therefore, there

is no surprise that a number of groups in recent years have worked in this field.[4–9] In the literature, the relationship between the amount of norbornene incorporated and the T_g is typically linear where in most cases a simple equation is quoted.[4–6]

As mentioned previously, it is believed that the thermal behavior of COCs is closely related to their microstructure, a quick indication of which is obtained using wide-angle X-ray scattering (WAXS). Several groups have worked in this field and observed the presence of two halos: an intense peak at 17° and a low-angle shoulder at 10 degrees.[1,3,10,11] The latter was attributed to the presence of norbornene blocks due to its similarity in the value of the angle that is observed with that of the WAXS pattern of polynorbornene.[12] The intensity of this peak typically increases with increasing norbornene content.

It is possible to find references concerning the dynamic mechanical behavior (DMTA) of norbornene/ethylene copolymers (COCs) dating as far back as 1974.[2] The recent advances in catalysis have meant the catalyst system employed nowadays have varied tremendously. Despite this difference those results can be used when comparing the results obtained in our work. Three relaxations were observed for certain COCs and termed as being the α, β, and γ relaxations. The former and latter relaxations are observed in all COCs; however, only in certain cases does the second relaxation manifest itself. The presence of the β relaxation was attributed to the presence of isolated norbornene units and their subsequent movements within the polymer backbone. It is worth noting that this assumption is still under debate. More recently work has been published concerning the DMTA behavior of COCs with low norbornene contents (11 mol %).[3] Akin to the initial study, three relaxations were observed. The presence of a third relaxation is related to the asymmetric form of the α relaxation. To further expand this work the behavior of copolymers having norbornene contents between 30 and 55 mol % are studied here.

The aim of this work is to examine the influence of the norbornene content on polymers prepared using rac-Et(Ind)$_2$ZrCl$_2$. The COCs are characterized using Differential Scanning Calorimetry (DSC), Wide-Angle X-ray Scattering (WAXS), and Dynamic Mechanical Thermal Analysis (DMTA). The combined use of these techniques is undertaken for the first time in this work, and permits a better approximation of the

Table I Polymers Studied by DSC and WAXD

Polymer	Norbornene Content (mol %)	Conversion (%)	T_g (°C)
First series			
A	0		—
B	40.7	18.8	110
C	46.9	6.1	131
D	51.8	2.1	153
E	52.2	3.0	161
Second series			
F	30.9	19.6	63
G	33.4	12.8	69
H	43.3	2.9	114
I	45.9	3.3	122
J	47.4	11.6	139
K	50.7	1.6	150

First series—100 mL toluene; second series—500 mL toluene in an autoclave.

influence the amount of and distribution of norbornene units have on the behavior of the polymer.

EXPERIMENTAL

Sample Preparation

Two series of polymers were synthesized using rac-Et(Ind)$_2$ZrCl$_2$, which is commercially available, and methylaluminoxane as the cocatalyst. The principle difference between each series was the size of reactor employed. The first series was synthesized employing the conventional Schlenk technique. In the second series an autoclave reactor was used to increase the quantity of polymer produced. The polymerization temperature was maintained at 30°C using a water blanket. The ratio of norbornene to ethylene in the reaction mixture was altered to change the amount of norbornene incorporated into the polymers. The amount of norbornene incorporated, measured by ^{13}C NMR in solutions of C$_2$D$_2$Cl$_4$ at 103°C, is shown in Table I. The polynorbornene, which is employed in this work as a reference, was prepared using a palladium catalyst rather than a metallocene catalyst.

A film of each polymer was prepared by compression molding using a Collin hot press. The polymer powder was placed between two teflon plates and heated to 170°C for 2 min. Throughout

this initial period no pressure was applied to the polymer to allow the polymer to melt and equilibrate at this temperature. A pressure of 50 bar was applied, and the sample held for a further 2 min at the same temperature. Both the teflon plates and film were then placed between two water-cooled plates to quench the sample.

DSC Measurements

Measurements were carried out on samples weighing between 5 and 10 mg using a Perkin-Elmer DSC7. A standard procedure was employed involving three heating cycles. The sample was first heated at a heating rate of 20°C/min from 20 to 200°C. This was followed by cooling the sample to the starting temperature at 20°C/min and a second heating cycle again at 20°C/min to 200°C to assure that all aging effects present in the first heating cycle were removed. The final temperature varied, depending on the glass transition temperature.

WAXS Measurements

Wide-angle X-ray diffractograms were recorded at room temperature using a Philips diffractometer with a Geiger counter connected to the computer. Ni-filtered Cu-K$_\alpha$ radiation was used. The trace was collected over a time period of 20 min between 2θ values of 3° and 43° using a sample rate of 1 Hz. The polymers studied are shown in Table I. The X-ray diffractograms were normalized to the same total intensity by dividing the values by the integral area of the spectra.

DMTA Measurements

The DMTA measurements were carried out on a Polymer Laboratories DMTA MkII apparatus. A typical experiment consisted of cryogenically cooling the sample, with liquid nitrogen, to -140°C followed by subsequent heating at a rate of 1.5°C/min to above its glass transition temperature. The length and thickness of the specimens typically varied between 15–18 mm and 250–400 μm, respectively, and their width was 2.2 mm. A tensile reducing force of 1 N was applied in a temperature range of -140 to 150°C. To allow the calculation of the apparent activation energy of each relaxation four frequencies were applied: 1, 3, 10, and 30 Hz.
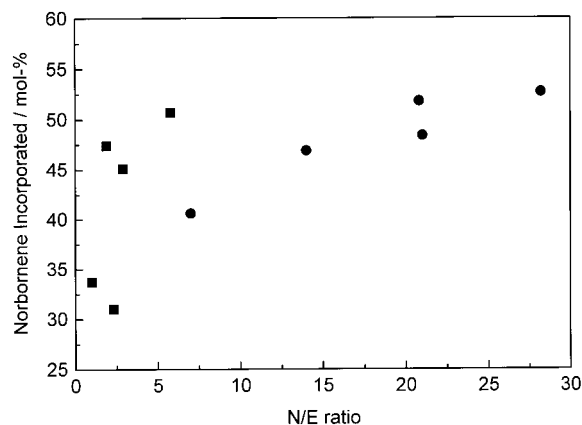
Figure 1 Variation of the norbornene incorporated with the ratio of norbornene to ethylene in the reaciton mixture. First series, ● second series, ■.

RESULTS AND DISCUSSION

Composition

Figure 1 shows that there is an increase in the amount of norbornene incorporated with increasing the N/E ratio. There is, however, a marked difference between the two series: by changing the reactor type a sharp increase appears in the amount of norbornene incorporated. Probably, the less effective heat transfer in the Schlenk experiments could produce a local increase of temperature, which leads to variations in the propagation rates of the comonomers. It was previously reported[5,10] that by increasing the ratio of norbornene to ethylene in the reaction mixture a maximum in the amount of norbornene incorporated is produced. Moreover, the catalytic activities of metallocene compounds in the polymerization of ethylene depend on certain parameters, such as Zr concentration in the reaction mixture, type of reactor, and stirring speed for the homogeneous catalyst,[13] anyone of which could have caused the differences observed.

DSC

Although the glass transition temperature of polynorbornene was found to be greater than 300°C,[14] the majority of the copolymers show only a glass transition temperature. This result indicates that COCs are predominantly random copolymers. The variation of the T_g with norbornene content, obtained from the second heating cycle, is plotted in Figure 2. A good linear correlation was obtained (correlation coefficient
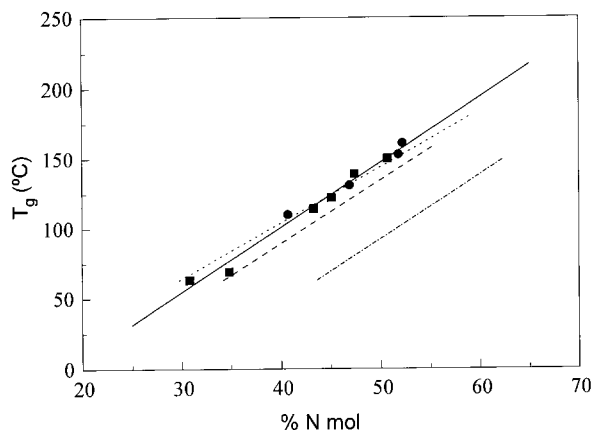
Figure 2 Variation of the glass transition temperature (DSC results) with the norbornene content: ●, first series; ■, second series; — best linear fit; – · – · –. Ref. 4, ... Ref. 5, - - - - Ref. 6.

>0.99): $T_g = -84.3°C + 4.64 \times$ mol % norbornene. The value of $-84.3°C$, although not exact, tends towards the T_g value of polyethylene. Also, in the case of polynorbornene, the T_g is calculated as being $380°C$, which is in fair agreement with values found in the literature.[12,14] As well as the experimental results obtained, Figure 2 also shows the graphical representation of other correlations, which have been found in the literature. That is,

$$T_g = (-354.4°C) \times (\text{wt} - \text{fraction ethene})$$
$$+ 216.8°C \quad \text{(Ref. 4)}$$

$$\text{mol } \% \ N = \frac{T_g}{4} + 14 \quad \text{(Ref. 5)}$$

$$\text{mol } \% \ Et = 79.72 - 0.2208 T_g \quad \text{(Ref. 6)}$$

The first observation, which can be made from Figure 2, is the scatter in the results obtained by the different groups. In a previous publication[15] we found that the catalyst system and, therefore, the microstructure, had a strong effect on the thermal behavior. This hypothesis would seem to be in agreement with the spread of results shown in Figure 2. The metallocene catalyst used in this work (rac-Et(Ind)$_2$ZrCl$_2$) is known to produce random copolymers[16] that typically display a linear relationship between T_g and composition. Our line in Figure 2 is comparable to the correlations proposed by Ruchatz et al.[5] and Brauer et al.;[6] however, it clearly varies from the correlation

proposed by Arndt et al.[4] A possible explanation for this difference is the slight differences in the microstructure and the amount of norbornene units that can be insinuated from wide-angle X-ray spectroscopy.

WAXS

The results of the two series are split into two graphs (Fig. 3), thus, it is easier to see how the scans vary with increasing norbornene content. All polymers showed two halos—one at 17.1° and a low-angle shoulder at 10°. The FWHM of the peak was measured as 4.5°, a similar value to that observed by other authors.[12] Although this is somewhat broader than a purely crystalline reflection, it is sharper than an amorphous halo, indicating a level of order intermediate in between the crystalline and amorphous phases.[17,18] A simple application of Bragg's Law gives an average distance between polymer chains of 5.2 Å. The maximum at 17.1° does not shift with copolymer composition for the range of copolymers studied. This would suggest that the COCs are random copolymers, which is a similar observation to that obtained from the DSC results. However, in the case of polynorbornene, the amor-
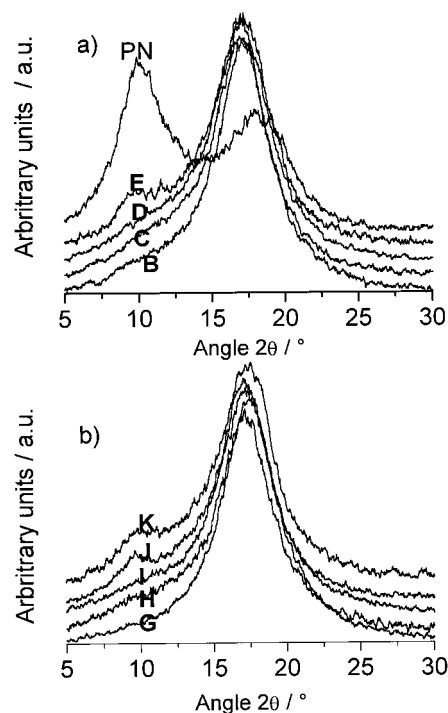
Figure 3 WAXD of polymers prepared using (a) first series, B to E samples and polynorbornene (PN). (b) second series, G to K samples.

phous maximum was observed[12] at 19°. This difference was attributed to the presence of more alternating sequences.

The low-angle shoulder was found to increase in intensity with increasing norbornene content [Fig. 3(a)] for the two series, owing to the fact that the low angle peak is more pronounced in pure polynorbornene. Moreover, the introduction of the ethylene comonomer reduces the height of the low-angle peak relative to the high-angle one[17] and this reduction was predicted by computer simulation[19] as well as experimentally found.[1] In addition to this, it has been suggested that the low-angle peak corresponds to the intermolecular spacing and the high-angle peak to the intramolecular spacing.[20]

The most important observation in the WAXD pattern is that in the sample with the higher T_g the low-angle shoulder is slightly more intense. This would insinuate that there are more blocks of norbornene present, resulting in an increased rigidity within the polymer backbone and thus increasing the T_g. It is expected that when adding more norbornene its unit will be less isolated and higher T_gs will be observed.

DMTA

Figure 4 shows the dynamic mechanical behavior of seven polymers with different norbornene contents, ranging from 0% (polyethylene) to 46 mol %. For simplicity, only seven sets of DMTA results are chosen; however, the general trends discussed here hold for the rest of the polymers. It should be noted that difficulties were encountered when preparing films with norbornene contents higher than 50 mol %. This was attributed to the fact that the polymers did not easily melt.

Prior to examining the DMTA results of the COCs it is necessary to look at those of the homopolymers. As polynorbornene is extremely brittle it was impossible to process the polymer and produce films. In linear polyethylene (PE) only two relaxations are observed: γ and α relaxations. The former occurs at around $-120°C$, and is attributed to local movements in the amorphous zone of polyethylene or other polymers with methylene or oxyethylene sequences containing at least three atoms, either C or O. The motions responsible of the γ relaxation are kink formation, inversion and migration.[21] The α relaxation in polyethylene takes place at around 50°C, and is associated to movements in the crystalline zone. Moreover, polyethylenes containing a significant
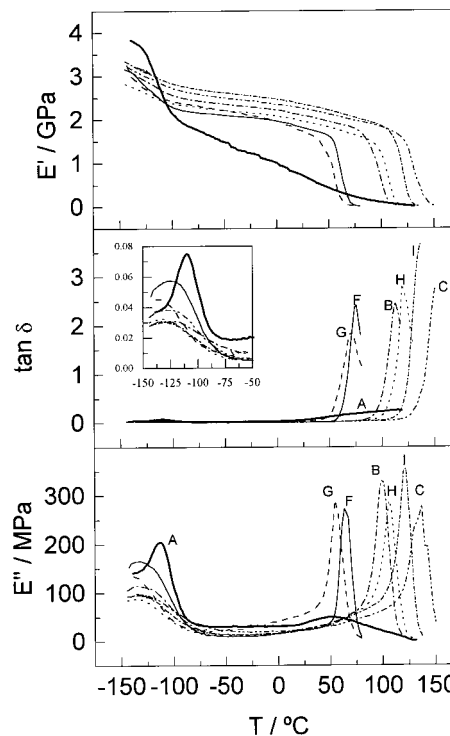

Figure 4 DMTA results.

degree of chain branching display another relaxation, the β one, at $-20°C$ approximately, which is usually related to the interfacial content of the polymers.

For majority of COCs studied in this work two relaxations are apparent and termed γ and α. At first, the former can be attributed to the presence of PE, and the latter to the glass transition temperature of the sample. However, the α relaxation had an asymmetric shape, reaching a low-temperature shoulder for the copolymers containing the lowest norbornene content. This would suggest the overlapping of a β relaxation produced by the interfacial content present in the copolymers. Samples with higher norbornene contents display a relaxation at 10°C, probably associated to motions of the norbornene ring.[2]

In general, for the tan δ curves, as the amount of norbornene incorporated increases, the relaxation at the lowest temperature (γ relaxation) decreases in intensity. This is consistent with the decrease in the amount of polyethylene present in the polymer backbone. Moreover, the position of the γ relaxation was shifted to lower temperatures as the norbornene content increased, and this behavior is also observed in copolymers of ethylene and α-olefins.[22] On the other hand, the

Table II   Apparent Activation Energies of Dynamic Mechanical Relaxations and T_g by DMTA at 3 Hz in tan δ

Samples	Activation Energy E_a/ (kJ · mol^{-1})		T_g tan δ, 3 Hz	%N mol
	γ	α		
A	105	145	—	0
F	50	>400	75	30.9
G	55	>400	71	33.4
B	50	>400	113	40.7
H	64	>400	119	43.3
C	60	400	149	46.9
I	58	>400	133	45.9

intensity of the α relaxation increases as norbornene does, due to differences in crystallinity. That is, for PE the intensity is typically 0.1, whereas for the COCs, this value increases significantly to values between 2 and 3, which are typical of a glass transition. As in the case of the DSC results, the amount of norbornene incorporated increased the temperature at which the glass transition temperature was measured. A result to be noted is that T_g values obtained by DMTA based on loss modulus plots are equal or somewhat lower than those obtained by DSC, unlike the customary behavior.

The storage modulus of PE is higher at very low temperatures compared with the COCs. With increasing temperature there is a crossover in the modulus of PE, which dips below that of the COCs. This feature can be explained by the incorporation of the bicyclic ring structure of norbornene, providing more rigidity to the polymer backbone. Moreover, Figure 4 shows a clear increase in the modulus with norbornene content. The influence of stereoregularity on storage modulus was reported by Harrington et al.,[8] who showed how the decay of the elastic modulus in a stereoregular COC has a shallow slope above its T_g compared to a random COC. In the present work this difference between semicrystalline and amorphous polymers appears clearly when comparing polyethylene and COCs, respectively (Fig. 4).

The apparent activation energy for each of the relaxations was calculated using the Arrhenius equation and their values listed in Table II. It can be concluded that the γ relaxation of ethylene–norbornene copolymers is produced by

secondary motions similar to those occurring in polyethylene. On the other hand, the high activation energy of the α relaxation of the copolymers (>400 kJmol^{-1}) leads to consider it as the glass transition, even though the same relaxation in polyethylene is produced by a different mechanism, movements in the crystalline region, and it has an apparent activation energy of 145 kJmol^{-1}.

CONCLUSIONS

The glass transition temperature measured by both DSC and DMTA was found to increase with the amount of norbornene content. The increase was found to be linear for the norbornene contents studied and the copolymers synthesized with the present catalyst. The fact that this catalyst gives random copolymers is supported by that linear relationship. When the results of this study are compared with those published in the literature, there is a certain degree of scatter between results. It is our belief that this is due to variations in the microstructure. That is, differences in the amount of norbornene blocks between samples will influence the rigidity and thus the glass transition temperature. The techniques used to measure the T_g are adequate for detecting slight microstructural changes in the copolymers.

REFERENCES

1. Kaminsky, W.; Arndt-Rosenau, M. In Metallocene Based Polyolefins: Preparation, Properties and Technologies; Scheirs, J; Kaminsky, W., Eds.; Wiley: New York, 2000, vol. 2.
2. Wilson, T. P.; Von Dohlen, W. C.; Koleske, J. J Polym Sci Polym Phys Ed 1974, 12, 1607.
3. Schulze, U.; Arndt, M.; Freidanck, F.; Beulich, I.; Pompe, G.; Meyer, E.; Jehnichen, D.; Pionteck, J.; Kaminsky, W. J Mater Sci Pure Appl Chem 1998, A35, 1037.
4. Arndt, M.; Beulich, I. Macromol Chem Phys 1998, 199, 1221.

5. Ruchatz, D.; Fink, G. Macromolecules 1998, 31, 4681.
6. Brauer, E.; Wild, C.; Wiegleb, H. Polym Bull 1987, 18, 73.
7. Henckschkle, O.; Köller, F.; Arnold, M. Macromol Rapid Commun 1997, 18, 617.
8. Harrington, B. A.; Crowther, D. J. J Mol Cat A: Chem 1998, 128, 79.
9. Bergström, C. H.; Sperlich, B. R.; Ruotoistenmäki, J.; Seppälä, J. V. J Polym Sci Part A Polym Chem 1998, 36, 1633.
10. Bergström, C. H.; Väänänen, T. L. J.; Seppälä, J.V. J Appl Polym Sci 1997, 63, 1071.
11. Rische, T.; Waddon, A. J.; Dickinson, L. C.; MacKnight, W. J Macromolecules 1998, 31, 1871.
12. Haselwander, T. F. A.; Heitz, W.; Krügel, S. A.; Wendorff, J. H. Macromol Chem Phys 1996, 197, 3435.
13. Quijada, R.; Rojas, P.; Narvaez, A.; Alzamora, L.; Retuert, J.; Rabagliati, F. M. Appl Cat A: Genl 1997, 1–7, 4027.
14. Reding, F. P.; Faucher, J. A.; Whitman, R. D. J Polym Sci 1962, 57, 483.
15. Forsyth, J.; Pereña, J. M.; Benavente, R.; Pérez, E.; Tritto, I.; Boggioni, L.; Brintzinger, H. H. Macromol Chem Phys 2001, 202, 614.
16. Galimberti, M.; Piemontesi, F.; Mascellani, N.; Camurati, I.; Fusco, O.; Destro, M. Macromolecules 1999, 32, 7968.
17. Ahmed, S.; Kohl, P.; Bidstrup, S.A.; Ludovice, P. Comp Theor Polym Sci 2000, 10, 221.
18. Mitchell, G.R. In Order in the Amorphpus State of Polymers; Keinath, S.E.; Miller, R. L.; Rieke, J.K., Eds.; Plenum Press: New York, 1987, pp 1–32.
19. Ahmed, S.; Bidstrup, S. A.; Kohl, P.; Ludovice, P. Makromol Chem Macromol Symp 1998, 133, 1.
20. Ludovice, P.; Ahmed, S. Van Order, J.; Jenkins, J. Macromol Symp 1999, 146, 235.
21. Heaton, N. J.; Benavente, R.; Pérez, E.; Bello, A.; Pereña, J. M. Polymer 1996, 37, 3791.
22. Cerrada, M. L.; Benavente, R.; Peña, B.; Pérez, E. Polymer 2000, 41, 5957.