

Influence of the Molecular Weight on the Thermal and Mechanical Properties of Ethylene/Norbornene Copolymers

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ABSTRACT: A series of ethylene–norbornene copolymers were synthesized using $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}t\text{Bu})\text{TiCl}_2$ as the metallocene catalyst and methylaluminoxane (MAO) as the cocatalyst, with the same molecular characteristics except the molecular weight, to evaluate its influence on the determination of the glass transition temperature (T_g). The polymers were characterized using wide-angle X-ray scattering, differential scanning calorimetry, microhardness measurements, and dynamic mechanical thermal analysis. The value

of the T_g for the same norbornene content and determined from the last three mentioned methods, increases significantly up to a limit of M_n about $6\text{--}10 \times 10^4$ (g/mol). Above this value, T_g remains practically constant. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3358–3363, 2003

Key words: catalysts; polyolefins; glass transition; mechanical properties

INTRODUCTION

The homopolymers of cycloolefins such as norbornene are not processable owing to the proximity of processing and degradation temperatures and their insolubility in common organic solvents. However, ethylene–norbornene copolymers do show thermoplastic behavior together with other interesting properties, such as excellent transparency and chemical, as well as solvent, resistance.¹ Due to the advances in metallocene catalysis, it is possible to control more efficiently the tacticity, molecular weight, and molecular weight distribution of the produced copolymers.² The nature and structure of the metallocene catalyst used,³ as well as the aluminoxane employed as a co-catalyst,⁴ influence the composition and microstructure of the final product.

So far, an extended variety of ethylene–norbornene copolymers has been synthesized, with the glass transition found in a wide range of temperatures, depending mainly on the content of the norbornene monomer. The most common relationship between the glass transition temperature (T_g) and the composition of these copolymers is linear, which has been shown by many groups.^{5–8} In a recent review⁹ of the equation that is derived from each working group, in addition

to results from our group, significant differences have been reported and attributed to small differences in the microstructure of the polymers, which result in significant discrepancies in the values of the T_g .¹⁰

The purpose of this work was to examine the influence of the molecular weight on the glass transition temperature of ethylene–norbornene copolymers prepared using $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}t\text{Bu})\text{TiCl}_2$ as the catalyst and methylaluminoxane (MAO) as the co-catalyst. To assure that the only parameter that is changing the T_g of the polymers is the molecular weight, the copolymers must have the same norbornene content, the same microstructure, and the same molecular weight distribution.

The polymers were characterized using differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), Vickers microindentation hardness (MH), and dynamic mechanical thermal analysis (DMTA). The combined use of these techniques permits one to obtain a more reliable conclusion about the influence of the molecular weight on the T_g of the copolymers. Moreover, it is possible to gather information regarding the molecular processes taking place in these polymers during the measurements and can be used to understand their behavior in different working conditions.

EXPERIMENTAL

All chemicals were handled and stored using a standard glove box and Schlenk techniques. $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}t\text{Bu})\text{TiCl}_2$ was obtained from the Boulder Scientific Co. (Mead, CO) and used as received, MAO was dried un-

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TABLE I
Molecular Characteristics of the Ethylene–Norbornene Copolymers Reported in This Study

Sample	X_N^a	$M_n \times 10^{-3}$ g/mol ^b	$M_w \times 10^{-3}$ g/mol ^b	M_w/M_n^b	$[\eta]$ (dL/g) ^b
ENW21	0.47	21	43	2.02	0.3022
ENW26	0.47	26	50	1.95	0.3333
ENW57	0.46	57	99	1.74	0.4352
ENW98	0.45	98	199	2.03	0.6861
ENW173	0.45	173	372	2.15	1.2353

^a Molar fraction of norbornene in the copolymer calculated from ¹³C-NMR.

^b Data obtained from SEC.

der a vacuum and stored as a powder, trimethylaluminum (TMA) was used as a neat liquid, and toluene was distilled over sodium under a nitrogen atmosphere. Norbornene was distilled over potassium under a nitrogen atmosphere and used as a stock solution in toluene. Ethene was passed over molecular sieves (4 Å) and BTS to remove oxygen and water.

The polymerization reaction took place as follows: To a thoroughly dried round-bottom flask (500 mL), a toluene and norbornene stock solution was transferred, to give the desired amounts of norbornene and a total liquid volume of 200 mL after addition of MAO and the catalyst. The stirring rate (1250 rpm), temperature (50°C), and ethene pressure (1.1 atm) were set and kept constant during the runs, and equilibration was allowed. Finally, TMA, MAO, and the catalyst were injected. TMA was used as a neat liquid whereas MAO and the catalyst were dissolved in toluene. The TMA:MAO ratio was varied to regulate the molecular weight, but the total amount of Al was kept constant [Al/Ti = 2000, $n(\text{Ti}) = 3.6 \mu\text{mol}$]. Polymerization was stopped by precipitation in an ethanol (2L)/HCl (40 mL) mixture, stirred overnight, filtered, stirred with ethanol overnight, filtered, and dried at 70°C under a vacuum.

For the ¹³C-NMR measurements, the copolymers were dissolved in C₂D₂Cl₄ with HMDS as the internal standard. The spectra were recorded on a Bruker AM-270 spectrometer operating at 67.89 MHz (¹³C) in the PFT mode operating at 103°C. Peak assignments and further experimental details were as reported earlier.¹¹

A high-temperature dual-detector size-exclusion chromatography (SEC) system GPCV2000 from Waters (Milford, MA) was used with two on-line detectors: a differential viscometer (DV) and a differential refractometer (DRI) as a concentration detector. The description of this SEC–DV system was reported elsewhere.¹² *o*-Dichlorobenzene + 0.05% 2,6-di-*tert*-butyl-4-methylphenol (BHT, antioxidant) was used as the mobile phase, at flow rate of 0.8 mL/min and a column temperature of 145°C. The column set was composed of three GMH_{XL}-HT columns from TosoHaas (Stuttgart, Germany). The universal calibration was constructed from 18 narrow MMD polystyrene standards, with the molar mass ranging from 162 to 5.48 × 10⁶ g/mol.

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 no more than 20 bar was applied to obtain thicker films, at the same temperature for a further 2 min. Both the Teflon plates and film were then placed between two water-cooled plates to quench the sample.

The DSC measurements were carried out on samples weighting between 5 and 8 mg, under a nitrogen atmosphere, using a Perkin–Elmer DSC 7 connected to a cryogenic cooling system. Every experiment involved three cycles: first, heating from 20 to 200°C at a heating rate of 20°C/min, followed by cooling the sample to the starting temperature at 20°C/min, and, finally, a second heating cycle at 20°C/min to 200°C.

Wide-angle X-ray diffractograms were recorded at room temperature using a Philips diffractometer with a Geiger counter, connected to a computer. Ni-filtered CuK α radiation was used. The scans were collected over a period of 20 min between 2 θ values of 3° and 43° using a sampling rate of 1 Hz. All diffractograms were normalized to the same total intensity.

Microhardness measurements were made by using a Vickers indenter attached to a Leitz microhardness tester. A constant load of 0.98 N was used, with a loading cycle of 25 s. The temperature was controlled with an external system and the sample was left to each temperature for 3 min to equilibrate. MH values (in MPa) were calculated according to the relationship

$$\text{MH} = 2 \sin 68 (P/d^2)$$

where P is the constant load (in N), and d , the diagonal length (in mm) of the projected indentation area.

Two different kinds of tests were conducted for the dynamic mechanical analysis. One was a tensile test with 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 the glass transition temperature. The length and thickness of the specimens typically varied between 15

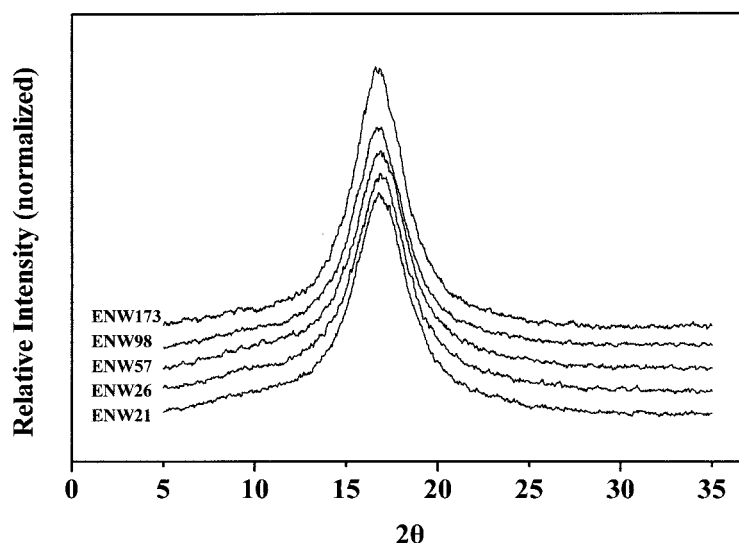


Figure 1 WAXS diffractograms for the ethylene–norbornene copolymers studied.

and 18 mm and 250 and 400 μm , respectively, and their width was 3.5 mm. A tensile force of 1 N was applied throughout the experiment. To allow the calculation of the apparent activation energy of each relaxation, four frequencies were applied: 1, 3, 10, and 30 Hz. The apparent activation energies were estimated according to an Arrhenius-type equation, from the temperature of the maximum values of $\tan \delta$ at the four mentioned frequencies.

Because of the fragility of the polymers in the tensile test, a single-cantilever bending test was also performed with a Rheometric Scientific DMTA V apparatus. The sample was then heated from 25 to 200°C with a heating rate of 1.5°C/min. The length of the sample measured was 2 mm, the width was kept to 3.5 mm, and the thickness varied from 300 to 600 μm . For the calculation of the apparent activation energy of each relaxation, four frequencies were applied: 0.1, 0.3, 1, and 3 Hz.

RESULTS AND DISCUSSION

The results of the molecular characterization are listed in Table I. From the molecular characteristics of the copolymers that were used for this study, it is evident that the only significant difference that they possess is the molecular weight. As for the microstructure, with the metallocene catalyst used, no significant amounts of norbornene blocks are observed.¹³

The WAXD patterns corresponding to the different samples are shown in Figure 1. Haselwander et al.¹⁴ found two peaks, located at $2\theta \sim 10^\circ$ and 19° , in polynorbornene homopolymers. The first peak was attributed to norbornene–norbornene blocks and this was confirmed with the work of Rische et al.,¹⁵ for ethylene–norbornene copolymers, where they observed that the intensity of the peak at 10° increases

with an increasing norbornene content. In this last work, they also reported the existence of a peak of higher intensity at 17° instead of the one at 19° . The position of this peak was invariant with the norbornene content and thus was attributed to the component common to all the ethylene–norbornene copolymers used, that is, the alternating sequences. From the WAXD of the samples in this present work, the presence of only one peak at 17° is apparent, due to the alternating sequences of ethylene and norbornene. Moreover, the diffractograms displayed in Figure 1 do not show the peak at 10° , confirming the absence of norbornene blocks in the samples studied.

Figure 2 shows the second heating cycle of a DSC experiment for one of the copolymers. The first heating cycle was not taken under consideration because it can be affected by aging phenomena that the sample may undergo. From the graph, we can see the appearance of only one glass transition temperature. This feature points out that the copolymers are not show-

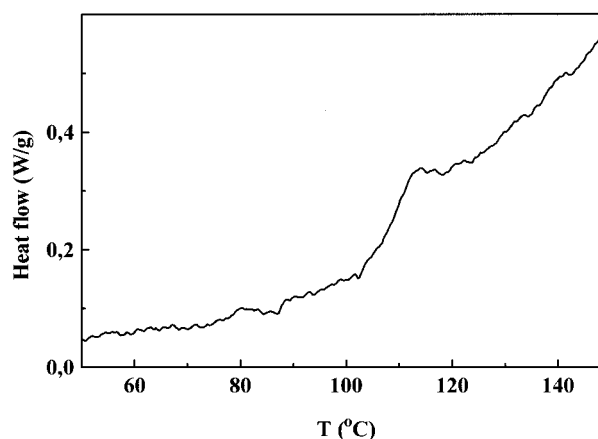


Figure 2 DSC second heating cycle of ENW21 sample.

TABLE II
Results from the Thermal and Mechanical Characterization of Copolymers

Sample	$M_n \times 10^{-3}$ g/mol	ΔH_γ^a (kJ/mol)	ΔH_α^b (kJ/mol)	T_g (°C) (DSC)	T_g (°C) (MH)	T_g (°C) ^b (DMTA)
ENW21	21	68	> 400	108	108	132
ENW26	26	66	> 400	111	111	134
ENW57	57	54	> 400	115	116	139
ENW98	98	62	> 400	119	118	145
ENW173 ^c	173	—	> 400	123	121	143

^a Calculated from DMTA in tensile mode.

^b Calculated from DMTA in single-cantilever bending test.

^c Due to lack of quantity of this sample, an experiment of DMTA in the tensile mode was not possible.

ing any signs of crystallinity and that they are homogeneous. The values of the T_g of each copolymer are reported in Table II. From these values, we can see that there is a small increase in the T_g with increase of the molecular weight, to a molecular weight of around 6×10^4 (g/mol), after which the increase in the T_g is insignificant.

To assure that this result is accurate, the T_g of the copolymers was determined by mechanical analysis. One of the ways utilized is the temperature dependence of the microhardness measurements. Sample preparation has a certain importance in microhardness tests. The films have to present a smooth surface and sufficient thickness to ensure that the hardness recorded is representative of the real plastic deformation of the material, without influence of the underlying substrate. The correlation between the elastic modulus and the microhardness was analyzed and verified previously.¹⁶ The variation of the MH with the temperature for the different samples is depicted in Figure 3. Two major observations can be made regarding the shape of the curves. The first one is that all the copolymers exhibit a small but noticeable decrease in the value of the MH around 50–60°C. As will be demonstrated also later, this “step” of the MH value can be

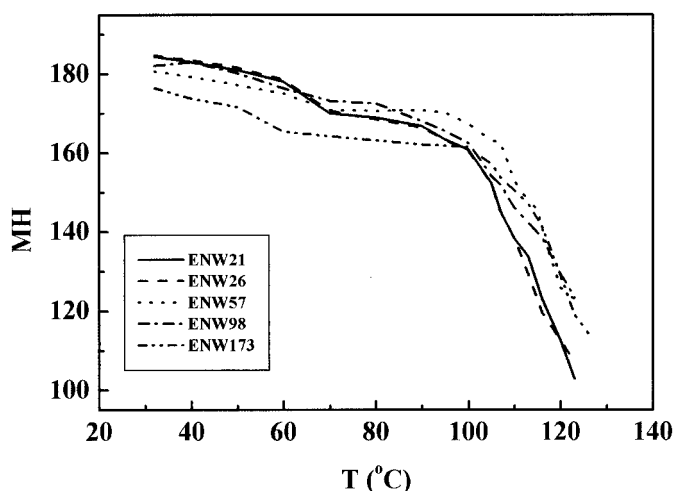


Figure 3 Variation of MH with temperature for the different samples.

attributed to the β relaxation of the copolymers. A big drop of the MH values at higher temperatures is also evident, which indicates the glass transition temperature as shown in an earlier work.¹⁷ The results of the microhardness measurements are reported in Table II, with the T_g taken as the point of the highest slope of the curves.

Prior to examining the DMTA results of the copolymers in a tensile mode, it is necessary to look at those of the “parent” homopolymers. The linear polyethylene presents only two relaxations, γ and α , at temperatures around -120 and 50°C , respectively. The γ relaxation is associated to kink inversion and migration in the amorphous region, taking place in a sequence of three or four ethylene units, and its activation energy is usually lower than 100 kJ/mol.¹⁸ More-

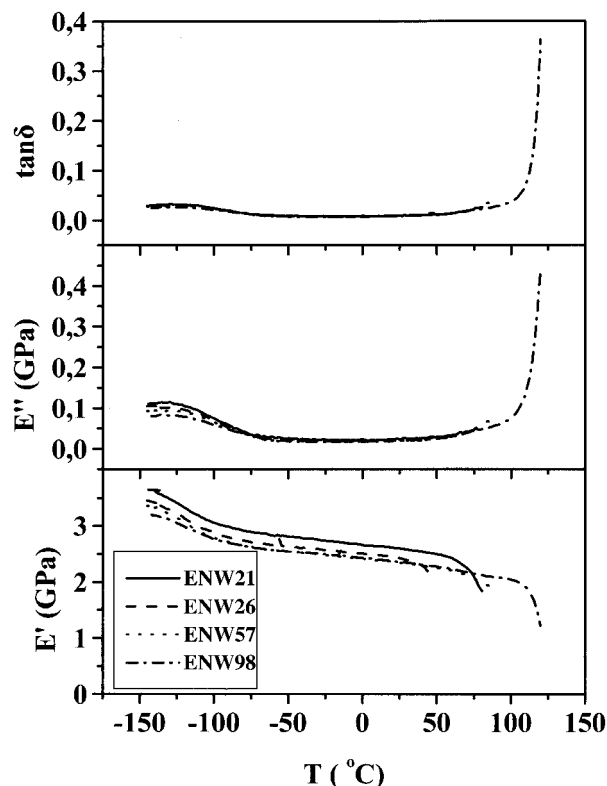


Figure 4 Variation of E' , E'' , and $\tan \delta$ with temperature in a tensile mode at 3 Hz, for the different samples.

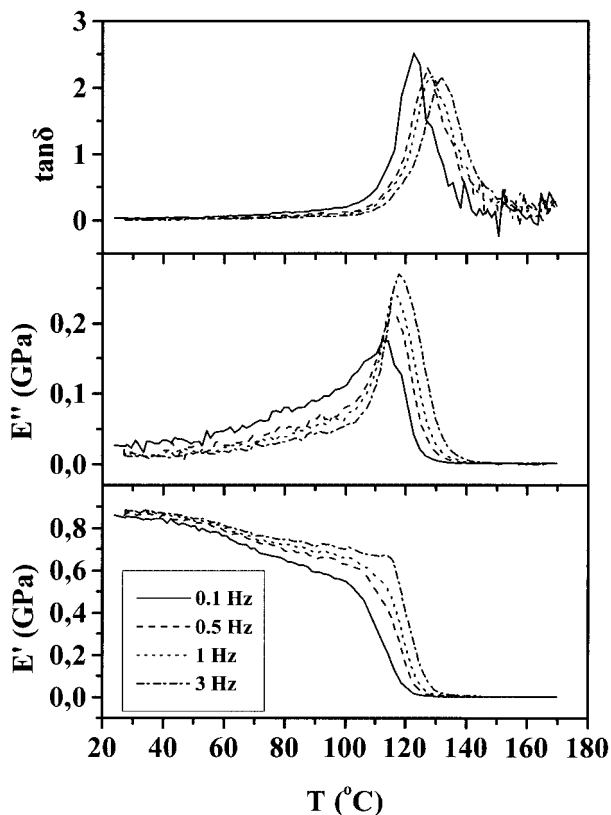


Figure 5 Variation of E' , E'' , and $\tan \delta$ with temperature, in a single-cantilever bending mode, at four frequencies for sample ENW21.

over, the α relaxation is well known to be due to crystal motions and its location depends on the degree of crystallinity and the size of the crystal. On the other hand, there is no report of measuring a polynorbornene homopolymer with DMTA because its film is very fragile.

The DMTA results of the copolymers studied, in a tensile mode and at frequency of 3 Hz, are shown in Figure 4. Three relaxations are observed, which will be called γ , β , and α , following an increase of temperature. The γ relaxation is observed at approximately -120°C and is connected to the γ relaxation of the polyethylene homopolymer, associated, as mentioned above, to motions of the ethylene units. The values of the apparent activation energy of the γ relaxation of the copolymers also correlates well with this assumption, as listed in Table II. It is evident that for all the copolymers it is almost the same and lower than 100 kJ/mol. The values of the storage modulus (E'), the loss modulus (E''), and the $\tan \delta$ at the temperature of the γ relaxation decrease according to the molecular weight. This feature could be expected since higher molecular weight creates a higher degree of entanglements and, therefore, more difficulty in the movement of the polymer chains.

The beginning of the glass transition is also indicated by a high drop of the values of the storage

modulus (Fig. 4). Unfortunately, all the samples are very fragile and they break before reaching the T_g . Moreover, from the storage modulus graph, a step in the values of E' around $50\text{--}60^\circ\text{C}$ can be noticed. Such a step appears in the graphs of E'' and $\tan \delta$ as a shoulder in the corresponding curves and it may be considered as the β relaxation. This relaxation seems to be associated to the norbornene unit and has been observed previously, in other ethylene–norbornene copolymers, with a medium or high norbornene content.¹⁹ It appears with very low intensity because of the hindered nature of the norbornene unit. The same relaxation was observed in the microhardness experiments as was mentioned before.

To establish the glass transition temperature, single-cantilever bending tests were made. A typical bending experiment of one of the samples, made at four frequencies, is shown in Figure 5. Since the experiment was conducted from 25°C , only the β and α relaxations are observed. It can be noticed that the β relaxation becomes more obvious at lower frequencies, since the rigid norbornene unit to which this relaxation was attributed has more time to move at these lower frequencies.

Figure 6 displays the results of the bending experiments at 3 Hz, showing that the α and β relaxations are detected in all the samples, even though the latter one is not so apparent in all the samples and can be

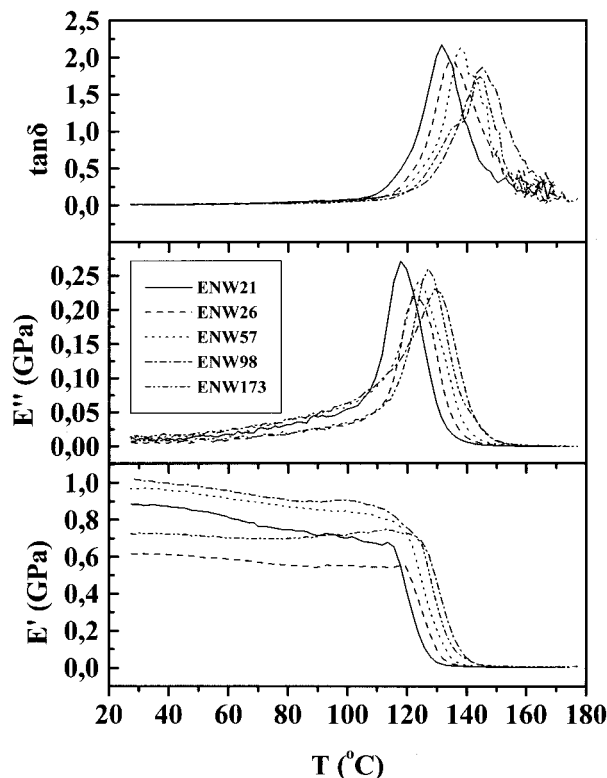


Figure 6 Variation of E' , E'' , and $\tan \delta$ with temperature, in a single-cantilever bending mode, at 3 Hz, for the different samples.

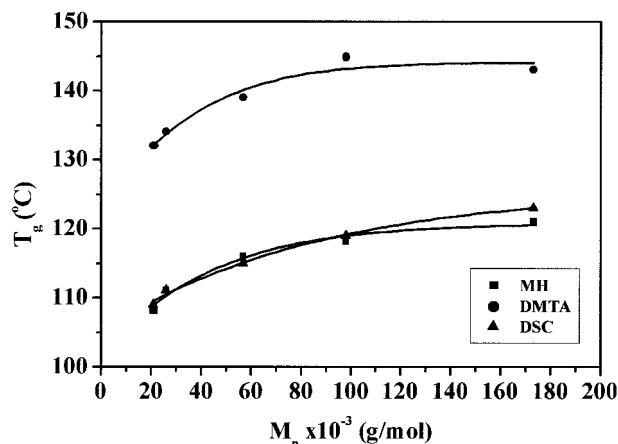


Figure 7 Variation of T_g values obtained from different methods, as a function of molecular weight of the copolymers

deduced from the asymmetric shape of the α relaxation. The length of the plateau in the E' graph increases according to the molecular weight, as can be expected because higher molecular weight signifies a higher number of entanglements.²⁰ The data derived from the bending experiments are listed in Table II. From the values of the apparent activation energy of the α relaxation, it is evident that this relaxation is really the glass transition temperature. The T_g is considered to be the maximum of the peak of $\tan \delta$. As for the β relaxation, there are no data derived because of the overlapping of the peak of this relaxation with the T_g peak.

Figure 7 presents the values of the T_g derived from the different methods, as a function of molecular weight (M_n). The shape of all three curves is similar and is constructed by an increase up to a limit around the value of $M_n = 6 \times 10^4$ g/mol, leading to a plateau at which the increase of the T_g according to the molecular weight is insignificant. As can be expected, the asymptotic trend of the curves resembles the Fox-Flory relationship²¹

$$T_g = A - (B/M_n)$$

The physical meaning of the constants A and B was discussed by Cowie and Toporowski,²² who found no further increase of the T_g above a critical value of the molecular weight. In the present copolymer samples, this value lies in the range from 6 to 10×10^4 g/mol. The higher values of the T_g derived from DMTA are considered normal because there is a frequency effect that shifts the mechanical T_g (3 Hz) more than 17°C higher than that of a DSC measurement (~ 0.0001 Hz).²³

CONCLUSIONS

There is an extensive literature referring to the increase of the T_g values of ethylene–norbornene copolymers according to the norbornene content. However, it seems there are also structural factors influencing the T_g value. One of these, the molecular weight of the copolymer, was examined in this work. From the results of three different methods of evaluation (DSC, MH, DMTA), it was shown that the values of the T_g , for the same norbornene content, increases significantly to a limit of M_n about 6×10^4 g/mol. Above this value, T_g remains practically constant.

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