**Full Paper:** This study involves research on possible relationships between the composition of ethylene/norbornene copolymers and their thermal properties. The copolymers were fully characterised by differential scanning calorimetry (DSC), ^{13}C NMR spectroscopy, Fourier transformation infra-red (FTIR) and Raman spectroscopy. The results of this study show that there is no linear correlation between the amount of norbornene incorporated in copolymers and thermal behaviour when copolymers containing high norbornene content and different microstructures are considered. The latter of which was found to be extremely sensitive to the catalyst used in its preparation.

Variation of glass transition temperature with norbornene incorporation.
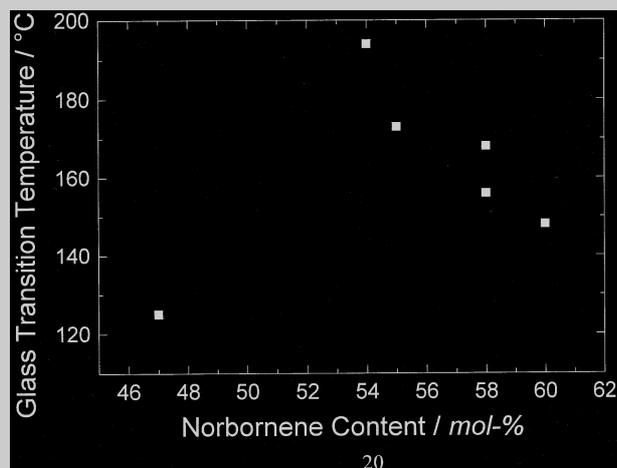
Influence of the Polymer Microstructure on the Thermal Properties of Cycloolefin Copolymers with High Norbornene Contents

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Introduction

Presently norbornene/ethylene (N/E) copolymers are semicommercially available from Hoechst (TOPAS) and Mitsui Sekka (APEL).[1] These cyclic olefin copolymers (COC) are typically synthesised using metallocenes and methylaluminoxane (MAO) based catalysts, a synthesis first reported in literature some years ago.[2–4] Their most interesting characteristics are high glass transition temperatures (T_g) and excellent optical properties, as a consequence of which these copolymers are used in heat-resistant and optical applications. In heat-resistant applications the high T_g necessarily requires copolymer microstructures containing high norbornene content in order to stiffen up the polymer backbone. This study is concerned with possible relationships among polymer composition, structure and thermal properties.

In the literature two principal hypotheses appear concerning relationships between glass transition temperature and the composition of the N/E copolymers. The most common of which is a linear relationship between norbornene content and T_g.[5–8] In most cases a formula is quoted relating glass transition temperature to norbornene content. An example of such a formula[8] is given below (Equation (1)).

$$\text{Norbornene content (mol-\%)} = (T_g/4) + 14 \qquad (1)$$

However, whether or not these relationships hold for all copolymers is placed in doubt by some results reported in literature. Indeed, copolymers with similar norbornene contents result in various glass transition temperatures. Harrington et al.[9] studied two copolymers with different microstructures: random and stereoregular/alternating microstructure. The results showed that copolymers with similar norbornene contents had significantly different glass transition temperatures. The stereospecific, alternating copolymers were found to be semi-crystalline
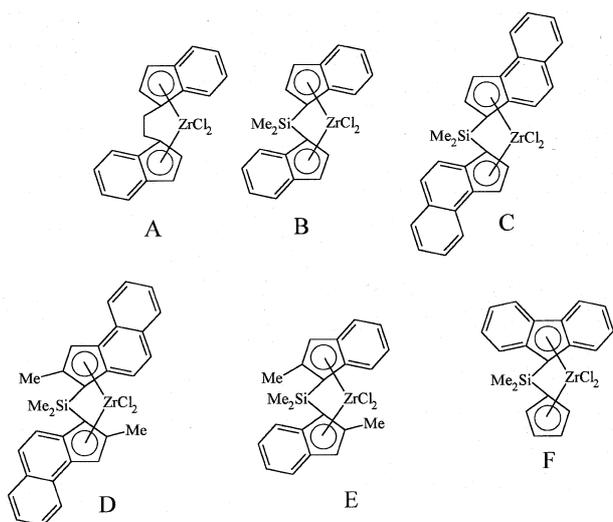
Figure 1.   Catalysts used in the synthesis of COCs.

(**C**), *rac*-Me₂Si(2-Me-B-[e]-Ind) ₂ZrCl₂ (**D**), *rac*-Me₂Si(2-Me-Ind)₂ZrCl₂ (**E**), all have C_2 symmetry whereas Me₂C-(Flu)(Cp)ZrCl₂ (**F**) is C_S symmetric.

The principle aim of this work was to try and obtain a correlation between the norbornene content and the thermal behaviour. This was achieved by characterising the COCs by differential scanning calorimetry (DSC), ¹³C NMR, Raman and Fourier transform infra-red (FTIR) spectroscopy.

Experimental Part

General Procedures

To prevent decomposition of the catalysts, all of the polymerisation steps were carried out under a dry nitrogen atmosphere by means of either a glove-box or using Schlenk line techniques. MAO (30 wt.-% in toluene, Witco) was used after previously removing the solvent and subsequently drying the resultant powder (50 °C) for 3 h in a vacuum (0.1 mm Hg). Toluene was dried and distilled from sodium under a nitrogen atmosphere. *rac*-Et(Ind)₂ZrCl₂ (**A**) and *rac*-Me₂Si(Ind)₂ZrCl₂ (**B**), were purchased from Witco, Me₂C-(Flu)(Cp)ZrCl₂ (**F**) was kindly provided by MONTELL and the rest of the catalysts were synthesised as part of the TMR network in the group of Prof. Brintzinger.

Polymerisation

Copolymers were synthesised using different metallocenes **A–F** activated by MAO. The polymerisation conditions were as follows: [Zr] = 8×10^{-5} mol/l, Al/Zr = 1 000, in 100 mL of toluene at 30 °C under ethylene atmospheric pressure. The copolymerisation reaction was stopped before 10% of the starting norbornene was consumed. Copolymers were fully characterised by ¹³C NMR spectroscopy. The activity and the norbornene content of copolymers obtained from a solution containing [N]/[E] = 24 and [N] = 3 mol/l are reported in Table 1.

Film Preparation

A film of each polymer was prepared by compression using a Collin hot-press. The polymer was initially held at 200 °C for 1 min between two teflon plates to allow the polymer to flow. Subsequently a pressure of 50 bar was applied for a further 2 min to produce the compressed film of the polymer. The resultant film was then cooled rapidly between two water-cooled plates, without applying any pressure.

DSC Measurements

The DSC measurements were carried out on samples weighing between 6 and 10 mg, under nitrogen, using a Perkin Elmer DSC 7, connected to a cryogenic cooling system. A typical experimental run involved three cycles: firstly heating from 20 °C to 200 °C at a heating rate of 20 K/min, followed by cooling the sample to the starting temperature at 20 K/min and finally a second heating cycle at 20 K/min to 200 °C.

with a glass transition temperature approximately 30 °C lower than their random counterparts. Moreover, a close observation of copolymers with identical norbornene contents, but synthesised using different MAO cocatalysts by Wang et al.,[10] shows that they have significantly different glass transition temperatures. The reason for which was quoted as being the result of differences in the polymer microstructures. Finally, Bergström et al.,[11, 12] hypothesised that the presence of blocks of norbornene along with alternating norbornene units result in higher T_g's due to an increased stiffness in the copolymer backbone. In conclusion, all these results insinuate that there are other factors which influence the glass transition temperature. That is, the glass transition temperature depends more on the microstructure, rather than solely on the norbornene content.

Recent studies carried out by Ruchatz et al.,[13] and this TMR network[14] have shown that the microstructure of these copolymers is dominated by metallocene, or more aptly by metallocene symmetry and ligand type, although the mechanistic details of the polymerisation are still unknown. Latest results have shown that the metallocene substituents and symmetry dictate the tacticity[14–16] and sequential distributions (blocky, random or alternating) of the ethylene-norbornene sequences in the copolymer backbone.

As a consequence of such differences in the microstructure and their influence on the overall behaviour of the COCs, a series of polymers with a relatively high norbornene content was synthesised using a number of different metallocene catalysts. These were specifically chosen to cover various aspects of catalysts design: ligand type, rigidity and symmetry (as seen in Figure 1). There are three bridge types: ethylene, —CMe₂— and —SiMe₂—. Metallocene catalysts *rac*- Et(Ind)₂ZrCl₂ (**A**), *rac*-Me₂Si(Ind)₂ZrCl₂ (**B**), *rac*-Me₂Si(B-[e]-Ind)₂ZrCl₂

Table 1. Glass transition temperatures and microstructures of ethylene/norbornene copolymers prepared using catalysts **A**–**F**. Conditions of polymerisation: [N]/[E] = 24, [N] = 3 mol/l, [Zr] = 8 · 10^{-5} mol/l, Al/Zr = 1 000, in toluene, 30 °C.

Catalyst	Sample name[a]	Activity kg/mol$_{Zr}$·h	norbornene mol-%	f_N (isol)	f_N (alt)	f_N (meso dyads)	f_N (blocks)	T_g °C
rac-Et(Ind)$_2$ZrCl$_2$ (**A**)	A55	2.04	55	+[b]	++	++++	++	173
rac-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**B**)	B58	1.20	58	+	+	++++	++	168
rac-Me$_2$Si(B-[e]-Ind)$_2$ZrCl$_2$ (**C**)	C54	1.62	54		+	++++	+	194
rac-Me$_2$Si(2-Me-B-[e]-Ind)$_2$ZrCl$_2$ (**D**)	D47	1.62	47	+	++++	+	+	125
rac-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$(**E**)	E60	1.74	60	+	++	++	++++	148
Me$_2$C(Flu)(Cp)ZrCl$_2$ (**F**)	F58	17.82	58	+	+++[c]	+++[d]		156

[a] The sample is named after the catalyst used in its preparation and the amount of norbornene incorporated.
[b] The number of crosses is indicative of the relative amount of the sequence distribution present.
[c] Isotactic and syndiotactic alternating sequences.
[d] Racemic ENNE sequences.

NMR Analysis

Solutions of the copolymer were prepared using $C_2D_2Cl_4$ as the solvent, with HMDS as an internal reference. The ^{13}C NMR was carried out on a Bruker AM-270 spectrometer at 67.89 MHz at 103 °C. The norbornene content was obtained using the following relationship.[15]

$$\text{mol-\% } N = \frac{1/3(I_{C2,C3} + I_{C1,C4} + I_{C7})}{(I_E + I_{C5,C6})} \times 100 \qquad (2)$$

where I_E + $I_{C5,C6}$ = integral of the signals between 26 and 30 ppm
I_{C7} = integral of the signals between 30 and 33 ppm
$I_{C1,C4}$ = integral of the signals between 34.5 and 41.6 ppm
$I_{C2,C3}$ = integral of the signals between 42.5 and 53.5 ppm

The molar fractions of the total norbornene content in isolated, isotactic alternating sequences, dyads and blocks (see Scheme 1), are defined as following
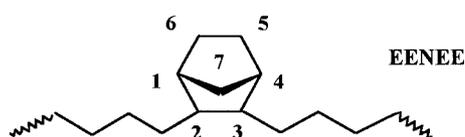
f_N(isolated) = EENEE + 1/2 EENEN,
f_N(alternating) = NENEN + 1/2 EENEN,
f_N(dyads) = 2 ENNE,
f_N(blocks) = blocks of three or more consecutive norbornenes

$$f_N(\text{blocks}) = f_N(\text{tot}) - [f_N(\text{isolated}) + f_N(\text{alternating}) + f_N(\text{dyads})] \qquad (3)$$

EENEE

Scheme 1.

FTIR and Raman Spectroscopy

FTIR and Raman spectroscopy were carried out on thin films of the polymer, prepared by compression using a Collin hot-press. The FTIR and Raman spectra were obtained using a Perkin Elmer FTIR spectrometer and a Jobin Yvon Raman

Spectrometer, respectively. In the case of the FTIR spectra films of a thickness less than 100 µm were used to prevent saturation of the absorption bands.

Results and Discussion

The results listed in Table 1 also include T_g and a qualitative distribution of the norbornene units (isolated, alternating, meso dyads and longer blocks), as measured from ^{13}C NMR analysis.

DSC Results

The results of the second heating cycle of the DSC run are shown in Table 1 and Figure 2. If the glass transition temperature is plotted against the amount of norbornene incorporated (mol-%) then Figure 3 is obtained. It is clear from Figure 3 that there would not appear to be any linear relationship between norbornene content and glass transition temperature for the range of norbornene content (47–60 mol-%) in the copolymers considered. In addition, the changes in T_g cannot be attributed to differences in the average molecular weights since COCs prepared
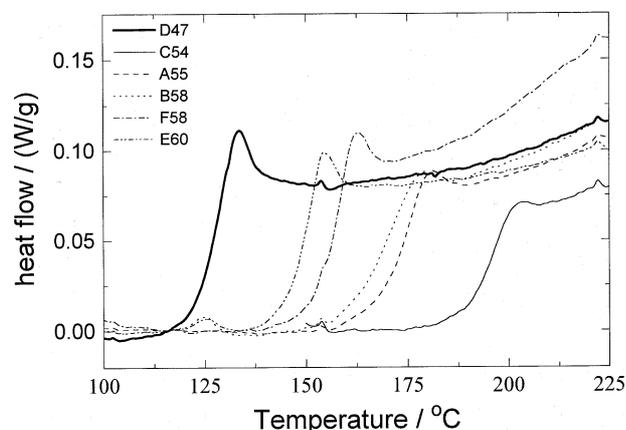

Figure 2. Results of DSC analyses. The polymers are displayed in accordance with increasing norbornene contents.
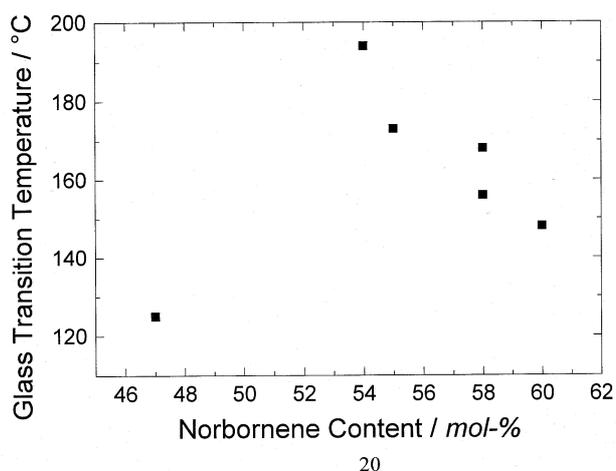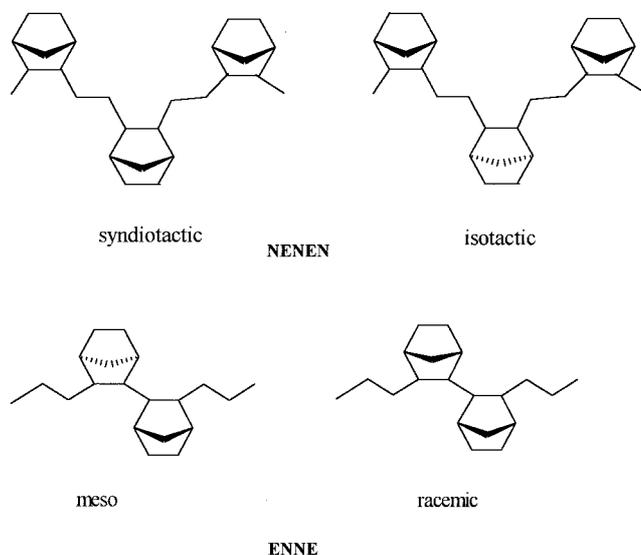
Figure 3. Variation of glass transition temperature with norbornene incorporation.

Figure 4. ^{13}C NMR spectra of the ethylene-norbornene copolymers prepared with *rac*-Et(Ind)₂ZrCl₂ (a), *rac*-Me₂Si(Ind)₂ZrCl₂ (b), Me₂C(Flu)(Cp)ZrCl₂ (c) and MAO cocatalysts. The spectra were measured in C₂D₂Cl₄ at 105 °C, chemical shifts are referred to HMDS.

^{13}C NMR

The non-linearity observed in Figure 3 can be understood better by considering the microstructure of each of the polymers. Previous results have shown that norbornene undergoes a cis-2,3 exo addition in ethylene-norbornene copolymerisation with metallocene catalysts (Scheme 1). However, the presence of two stereogenic carbon atoms on the polymer chain makes possible the synthesis of various NENEN alternating and ENNE stereosequences as shown in Scheme 2. The signals of such stereochemical environments have been observed in the ^{13}C NMR spectra of COCs and the assignment of these peaks are encoun-
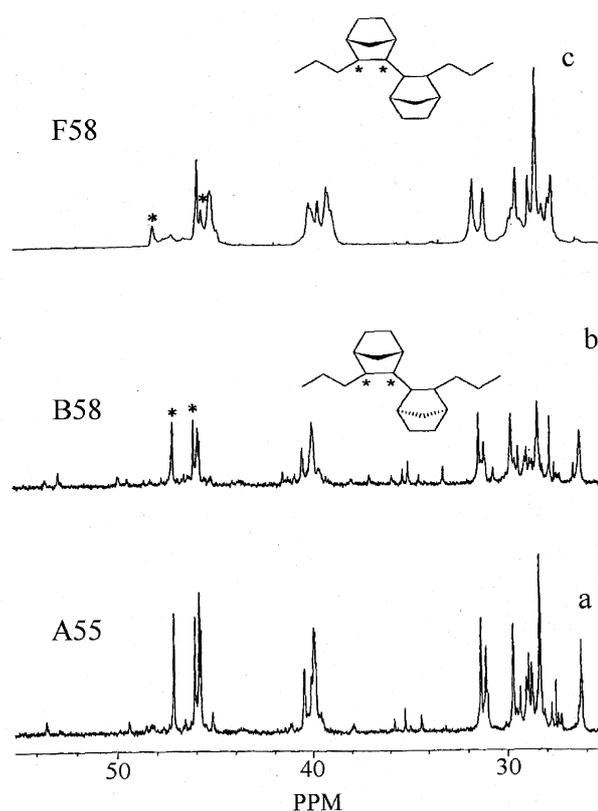
tered in the literature.[14, 15, 17] On the other hand, the assignment of the signals corresponding to norbornene triads and longer blocks is not available.

The ^{13}C NMR spectra of the copolymers studied are shown in Figure 4 and 5. In Figure 4 the spectra of copolymers prepared with two C₂ symmetric catalysts, *rac*-Et(Ind)₂ZrCl₂ (**A**, Figure 4a), *rac*-Me₂Si(Ind)₂ZrCl₂ (**B**, Figure 4b) which differ only in the bridge between the two indenyl ligands, and with the Cₛ Me₂C(Flu)(Cp)ZrCl₂ (**F**, Figure 4c) are shown. The spectra of the copolymers obtained using the other three C₂ symmetric metallocene catalysts *rac*-Me₂Si(B-[e]-Ind)₂ZrCl₂ (**C**), *rac*-Me₂Si(2-Me-B-[e]-Ind)₂ZrCl₂ (**D**), *rac*-Me₂Si(2-Me-Ind)₂ZrCl₂ (**E**) are seen in Figure 5a, 5b, and 5c, respectively. The ethylene-norbornene sequences most characteristic of each spectrum are also depicted in Figure 4 and 5.

The microstructure of the COCs was found to be strongly dependent on the symmetry of the catalysts and on the Cp substituents, as is apparent from the different patterns of the spectra in Figure 4 and 5. The spectrum of the COC prepared with catalyst **D** (Figure 5a) is typical of a copolymer with a microstructure consisting of almost entirely isotactic alternating NENEN sequences. There are five main peaks at 28.39, 31.06, 40.04, and
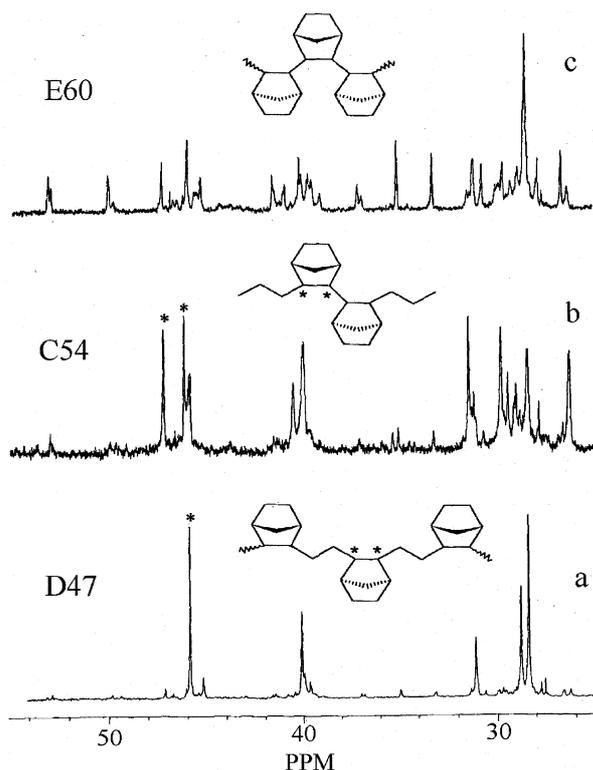

syndiotactic **NENEN** isotactic

meso **ENNE** racemic

Scheme 2.

Figure 5. ^{13}C NMR spectra of the ethylene-norbornene copolymer prepared with *rac*-Me$_2$Si(B-[e]-Ind)$_2$ZrCl$_2$ (a), *rac*-Me$_2$Si(2-Me-B-[e]-Ind)$_2$ZrCl$_2$ (b), and *rac*-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$ (c), and MAO cocatalysts. The spectra were measured in C$_2$D$_2$Cl$_4$ at 105 °C, chemical shifts are referred to HMDS.

45.82 ppm that correspond to C5/C6, C7, and C2/C3 norbornene carbons, respectively, and 28.74 ppm of an ethylene unit. The signal at 45.82 ppm due to the C2/C3 carbons gives the most direct information concerning the sequence tacticity. The copolymer prepared with catalyst **C** which is mainly meso dyads, as revealed from the presence of two pairs of signals at 26.24 and 29.68 ppm, and 46.04 and 47.12 ppm, which can be assigned to C5/C6 and to C2/C3 carbons in the meso ENNE sequence. The copolymer prepared with catalyst **E** contains the greatest amount of longer blocks. The COCs prepared by using the other two C$_2$ symmetric metallocene catalysts, **A** and **B**, are made up of mixtures of alternating sequences, meso dyads and blocks of three or more norbornenes. The ENNE meso sequences prevail over longer norbornene blocks. This is apparent from the comparison of the intense pair of signals at 46.04 and 47.12 ppm of the dyad with the other small signals in this part of the spectrum e.g. those at 53.45 and 49.36 ppm arising from C2/C3 methine carbons of longer norbornene blocks.

The polymer synthesised using catalyst **F** contains signals of alternating sequences and racemic norbornene ENNE. The pairs of signals observed at 27.58 and 29.37 ppm, and 46.02 and 48.07 ppm, correspond to carbons C5/C6 and C2/C3 in the racemic ENNE sequence, respectively.

Such differences in copolymer microstructures are qualitatively represented in the last three columns of Table 1 by giving the relationships between the molar fractions of norbornene in alternating sequences, dyads, or longer blocks.

Even though copolymers may have similar norbornene contents, there are three distinct microstructures, which can be present. The mainly alternating copolymer shows the lowest T_g. The meso dyads significantly increase the glass transition temperature, as seen by comparing the T_g of A55 (173 °C), prepared with metallocene **A**, with that of C54 (194 °C), a copolymer prepared with metallocene **C**, which mainly made up of meso ENNE sequences. This may be attributed to the norbornene dyads causing an increased tension and subsequent rigidity in the polymer backbone.[17] The copolymer with the highest content of alternating sequences has the lowest T_g because of its lower rigidity. Among the COCs containing dyads or longer norbornene blocks, the copolymer with the highest amount of blocks, E60, yielded the lowest T_g (148 °C). Although this copolymer has the highest norbornene content, this observation shows that it is not only the norbornene content which influences the thermal behaviour but the distribution of the norbornene unit (alternating sequences or dyads and triads with various stereoregularities). A more detailed analysis of the influence of norbornene sequence length on T_g cannot be attempted in this paper because the number of EN dyads in these samples is very high when the samples contain either a large amount of alternating sequences (-NENEN-) or norbornene dyads (ENNE).

FTIR Measurements

From the results of ^{13}C NMR it was evident that all of the COCs contained a certain level of isolated norbornene (corresponding to the EENEE pentad). This is confirmed by FTIR spectroscopy. From Figure 6 it is clear that all of the COCs show an absorption peak at 720 cm^{-1}, which can be assigned to the presence of 4 or more CH$_2$ units.[18] Again as in the case of the results of the ^{13}C NMR, the different symmetry of catalyst (**F**) makes the spectrum of F58 quite different from those of the rest of the COCs.

Raman Spectroscopy

In addition to the six polymers studied in this report the Raman spectra of both polyethylene and polynorbornene are included. The catalysts used in the preparation of these polymers were **A** and **D**, respectively. It was hoped that the differences between these spectra could give rise to bands which were characteristic of the norbornene/ethylene copolymer.
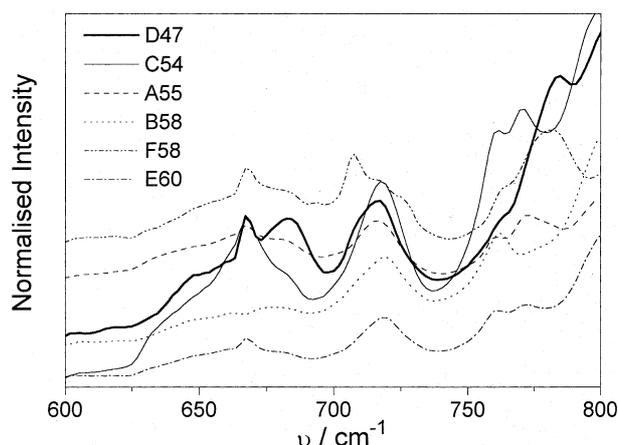
Figure 6. FTIR spectra of the COCs. The polymers are displayed in accordance with increasing norbornene contents.
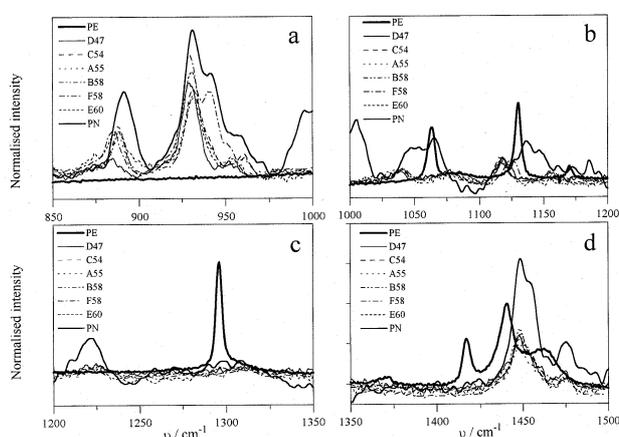

Figure 7. Raman spectra of COCs. a: 850–1000 cm^{-1}; b: 1000–1200 cm^{-1}; c: 1200–1350 cm^{-1}; d: 1350–1500 cm^{-1}. The polymers are displayed in accordance with increasing norbornene contents.

To simplify the interpretation, the fingerprint region of the spectrum, between 850 and 1500 cm^{-1} is divided into four different parts (Figure 7). To obtain comparative results each spectrum is normalised. The signal to noise ratio of the corresponding polynorbornene spectra is significantly greater than the rest of the polymers as the spectra were obtained from a powder sample, whereas the other spectra were obtained from a film.

In the region from 850 to 1000 cm^{-1} (Figure 7a) no bands arising from PE are found. Therefore it can be assumed that the strong bands observed at 880, 920 and 930 cm^{-1} are of norbornene units. The band at 880 cm^{-1} has approximately the same intensity for all the COCs, with the exception of that of D47. This copolymer has the lowest norbornene content and glass transition temperature, but the most important factor is that it is composed of almost entirely alternating sequences. The rest of the copolymers have similar norbornene contents and amounts of blocks of norbornene units (i.e., meso dyads,

racemic dyads, blocks), even though it should be stated that the types of block vary for each polymer. A possible relationship between the intensity of the band at 880 cm^{-1} and the norbornene content is not conclusive. This band was found to increase in intensity with the amount of norbornene incorporated, for propylene/norbornene copolymers.[19]

The two other bands in this region, 920 and 930 cm^{-1}, may be related to the configuration of the norbornene units. The COCs prepared using the catalysts with a C$_2$ symmetry have similar intensities. However, the only polymer synthesised using a catalyst with a different symmetry is F58. If the spectrum is compared with those of the other COCs there is a marked difference in the intensity of the band at 930 cm^{-1}. The shape is very similar to that of the norbornene homopolymer. The results of ^{13}C NMR showed that F58 was made up of isotactic and syndiotactic alternating sequences along with racemic dyads of norbornene. To assign this peak to anyone of these configurations it is necessary to carry out further work with differing amounts of each of the sequences.

In Figure 7b the region from 1050 to 1100 cm^{-1} corresponds to the skeletal stretching region of the C—C—C bonds in PE. The crystalline and amorphous bands of PE are observed at 1062 and 1080 cm^{-1}, respectively. In this region the only band which is present is that of 1080 cm^{-1}, which was fully expected as the polymers are completely amorphous.

The region of the spectrum observed in Figure 7c corresponds to the torsion movements of CH$_2$ groups. There are two characteristic bands of each of the homopolymers: 1225 cm^{-1} related to polynorbornene and 1295 cm^{-1}, which is normally taken as the reference band of PE. In the case of the COCs only the former of the two bands is evident, which confirms the absence of blocks of polyethylene.

In Figure 7d the sharp band at 1416 cm^{-1} in the PE sample is characteristic of an orthorhombic crystal structure. The subsequent absence of this band in the COC samples insinuates that there is no crystallinity within the samples related to the presence of PE.

Conclusions

The results of this study show that the microstructure of the COCs plays an important role in the thermal properties. Polymers which contain high norbornene contents do not necessarily have higher glass transition temperatures, for example the low T_g found for E60. In the case of copolymers made up of predominantly alternating/isolated norbornene, the T_g measured is relatively low. This can be attributed to the increased flexibility in the polymer backbone. The reverse situation is also observed. That is, polymers where longer norbornene sequences predominate have higher T_g's due to the increased stiffness introduced

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in the polymer backbone. It should be noted that not only the presence of a type of sequence but also the stereoregularity of the different chain segments seem to affect the copolymer's T_g. It is also clear from the results that the microstructure of the COCs is extremely catalyst sensitive. Among the C_2 symmetric catalysts **C**, **D** and **E**, *rac*-Me$_2$Si(2-Me-B-[e]-Ind)$_2$ZrCl$_2$ (**D**), with bulky benzo and methyl substituents in the 4, 5 and 2 positions, produces a mainly isotactic alternating microstructure, whereas the *rac*-Me$_2$Si(B-[e]-Ind)$_2$ZrCl$_2$ (**C**) catalyst, which has only the benzo substituent, yields COCs containing predominantly meso dyads. The *rac*-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$ (**E**) gives a blocky microstructure, i.e. the highest amount of norbornene in microblocks with more than two consecutive norbornene units. Finally, the results of this work lead to the conclusion that there does not appear to be a linear correlation between the amount of norbornene incorporated and the T_g measured when copolymers with high norbornene content and different microstructures are considered.

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