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Chain features and their influence on the thermal stability of poly(propylene-co-1-nonene) copolymers --Manuscript Draft--

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Full Paper

Chain features and their influence on the thermal stability of poly(propylene-*co*-1-nonene) copolymers

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ABSTRACT

The thermal stability of several isotactic polypropylenes and propylene-*co*-1-nonene copolymers is assessed under nitrogen by means of TGA. The samples involve wide ranges of molecular weight, isotactic average length and 1-nonene content, in order to perform a comprehensive analysis of the effect that chain features exert on the apparent activation.

The degradation process correlates with chain mobility and, accordingly, with chain features that are linked to. Thus, microstructure and chain size are found to play a key role. In fact, isotactic average length of propylene sequences and molecular weight are driving factors in the E_a required for main chain thermal scission.

1. INTRODUCTION

Polymeric materials are irreplaceable in many today's applications, either of high performance or of daily use. This fact is mainly grounded in their macromolecular character. Aside from the enormous diversity of monomers available, an essential requirement is to obtain a molecular weight high enough to combine an optimal mechanical behaviour with other specific properties, associated with the distinctive functionality of the monomers together with the resulting chain microstructure. Thus, the noticeable presence of sequence lengths at a specific composition or at a characteristic stereo-configuration, or at both together, in macrochains with molecular weights sufficiently high, are the features that determine the selective intra and inter-chain arrangements, conferring unique properties to these materials in the solid state.^[1,2]

Maintenance of the molecular weight in polymers is, consequently, of primary importance to prevent the loss of their original performance. This objective starts in polyolefins in the stage of material processing and involves the use of thermal stabilisers. Thus, very few chain scission processes, occurring in presence or absence of oxygen, can lead to greatly shorten the macrochain size.^[3-5] The mentioned additives act, however, "a posteriori" when some incipient radical activity has been already initiated.^[6,7] Therefore, the challenge is how to circumvent the occurrence of those initial chain breakages in the molten state.

The case of the isotactic Polypropylene (PP) is a paradigm. As a matter of fact, there exist some local low- E_a degradation processes^[8-13] that cause chain scissions during the melt processing and, inevitably, lead to a loss of properties. This phenomenon is undoubtedly related to the presence of certain labile structures and not to rheological aspects of the melting process, like an enhanced diffusion of the generated radicals, since the apparent E_a of the degradation would have to decrease with temperature, because of the reduction in viscosity.

Quite on the contrary, dynamic TGA studies show that the energy required for chain scission increases as temperature range is raised.^[8-13]

There is not agreement about its origin although the phenomenon is well documented. It has been generally ascribed to the existence of chemical defects, as oxygen containing groups.^[8-10] Some previous works have indeed shown that these structures are really involved from the very beginning of degradation. In particular, there is some qualitative FTIR and ¹H NMR evidence about the vanishing of carbonyl species when the material has hardly lost 1 wt%.^[12,14] Nevertheless, the apparent E_a of the degradation remains quite low up to losses close to 10 wt%, when those anomalous structures have been already vanished and the scission of regular chain bonds is the main degradation event.

These chain scissions, from anomalous chemical structures, can be only prevented by controlling the reaction conditions used during polymerization.^[15] On the contrary, other breakages from regular main-chain units, with low E_a , could be avoided or, at least predicted, by knowing the factors associated with the presence of the so-called “weak points”. Previous results showed a significant increase, just at the beginning of the pyrolysis, of the isotactic average length that indicated the involvement of some specific non-isotactic units.^[12] Next, the increasing trend of the apparent E_a with the weight loss was ascribed to both the contribution of shorter isotactic sequences and the reduction of molecular weights.

Large molecular weights have been also found to play additionally a specific role in the energy required for early chain scissions. High chain lengths actually promote the existence of both inter and intra-molecular chain interactions where stresses, resulting from high frequency dynamics in the molten state, are concentrated.^[12,14] Then, a general picture of the initiation of PP pyrolysis must consider factors affecting chain mobility. In particular, the whole chain length (*i.e.* the chain molecular weight), the average sequence length, defined by either the

composition or the stereo-configuration, or for both of them, since they determine whether chains are able to convert the supplied energy into chain motions (inter or intramolecular) or in chain breakages. A prior exploratory study on the evolution of the E_a in the pyrolysis of propylene copolymers with both 1-pentene and 1-hexene^[16] suggests that, chain mobility drives the energy requirements of the process.

This work proposes to check the validity of this hypothesis by studying the thermal stability of propylene based copolymers, whose isotacticity interruptions are the comonomer units, which confer enhanced inter and intra chain mobility. In particular, four series of (propylene-*co*-1-nonene) copolymers, synthesised at different temperatures, and with different 1-nonene (C₉) contents (up to about 12 mol.%) will be considered.

2. EXPERIMENTAL PART

2.1. Materials

Toluene (Merck) and the comonomer 1-nonene (C₉) (TCI Tokyo Kasei) were previously refluxed over sodium, distilled and kept under N₂ to avoid the presence of water traces and oxygen. Both propylene (Praxair 2.5) and nitrogen (Praxair 3X) were passed through oxygen-trap columns and molecular sieves before using. The catalyst *rac*-dimethylsilylbis(1-indenyl) zirconium dichloride (Strem) and the modified methylaluminoxane (MMAO) cocatalyst (solution in toluene, 7 wt% in Al from Aldrich) were used as received. The activated catalyst was prepared by dissolving 17 mg of the metallocene in 3 mL of MMAO solution. Ethanol (Aroca, 96%) and HCl (VWR, 37%) were used for the precipitation of the polymers.

2.2. Synthesis and processing of samples

Homo and copolymerisations of propylene with C₉ were carried out in a 500 mL Büchi glass Ecoclave at -5, 10, 25 and 60°C in toluene (250 mL) by using *rac*-dimethylsilylbis(1-

indenyl)zirconium dichloride/MMAO as the catalyst/cocatalyst system ($[Al]/[Zr]=1925$). The initial propylene pressure was 1.5 bar, the catalyst amount was $4.04 \cdot 10^{-6}$ mol and the starting C_9 /propylene molar ratio ranging from 0 to 0.5. The copolymerisation reaction was stopped at 10% of propylene consumption by adding 5 mL of ethanol and enabling the unreacted propylene out from the reactor. Polymers were obtained as powders by pouring the reaction batch on a mixture of ethanol/HCl (30:1). The precipitated solid was stirred thoroughly overnight, filtrated, washed again with ethanol and, afterwards, dried under vacuum at room temperature. Table 1 shows the different materials prepared, which are referred for the copolymers as CP followed by the polymerisation temperature ($T^{polymerisation}$) and the closest integer value for the C_9 mol.% content. The iPP homopolymers are simply identified by their corresponding $T^{polymerisation}$.

Films of the homo and copolymers were obtained by compression moulding in a Collin press between hot plates, at a temperature of 30 °C above their corresponding melting points, at a pressure of 2 MPa, for 3 min. The subsequent cooling down to room temperature was performed between refrigerated plates under the same pressure.

2.3. 1H and ^{13}C NMR analysis: Molecular weight and microstructure in composition and configuration

The 1H and ^{13}C NMR spectra of copolymers were obtained by using a Bruker 400 spectrometer from solutions of the samples in 1,1,2,2-tetrachloroethane- d_4 (70 mg / 0.7 mL) at 80 °C. For PP samples, 1H and ^{13}C NMR spectra were obtained with a Bruker Avance III HD-500 at 100°C. ^{13}C NMR spectra were recorded with broad band proton decoupling, using a 24,038 Hz spectral window, an acquisition time of 1.15 s, a relaxation delay of 5 s, a pulse angle of 45° and a minimum of 8000 scans. The 1H NMR spectra, in turn, were performed by accumulating 64 scans. The shortest proton spectrum was obtained always prior to the ^{13}C

one, to avoid the appearance of signals caused by processes associated with long residence times of the ^{13}C NMR analysis, like degradation and isomerization of end chain double bonds.^[17-19]

Table 1. Characteristics of samples: C_9 content, number-average molecular weight determined by ^1H NMR and SEC, polydispersity (PDI) and melting temperature.

Sample	$T^{\text{polymerisation}}$ (°C)	C_9 content (mol%)	^1H NMR	SEC		T_m (°C)
			M_n $\text{g}\cdot\text{mol}^{-1}$	M_n $\text{g}\cdot\text{mol}^{-1}$	PDI	
PP-5	-5	0	--	38700	4.54	151.0
CP-5_2		2.2	27400	--	--	123.0
CP-5_3		2.8	18100	--	--	118.5
CP-5_4		4.2	19800	--	--	110.0
CP-5_5		4.8	18000	--	--	104.5
CP-5_6		6.2	--	--	--	95.5
CP-5_8		8.0	12500	--	--	84.0
PP10	10	0	38200	39200	3.67	149.0
CP10_2		2.3	32600	--	--	123.5
CP10_4		4.0	23300	--	--	110.5
CP10_7		6.6	14000	--	--	92.5
CP10_9		9.3	12400	--	--	75.0
PP25	25	0	29000	34500	2.86	145.5
CP25_2		2.3	22500	--	--	120.5
CP25_5		5.1	16800	--	--	99.0
CP25_8		8.2	14200	--	--	88.5
CP25_11		11.2	10800	--	--	66.0
PP60	60	0	8600	--	--	131.0
CP60_2		2.4	9700	--	--	112.5
CP60_5		5.1	13900	--	--	97.0
CP60_8		7.6	9600	--	--	78.5
CP60_8bis ^a		7.7	5900	--	--	76.5
CP60_12		11.9	6800	--	--	54.5

a) Sample with the same C_9 integer value but lower molecular weight than the preceding one.

The molar content in C₉ for the different copolymers is listed in Table 1. It was estimated from the relative intensities of the methyl signals at 14.08 ppm (C₉) and 19.4–22.0 ppm (propene) in the ¹³C NMR spectrum. The so-obtained compositions were compared with those ones calculated from the methine carbons, and no appreciable differences were found. Additionally, the comonomer distribution at the triad level as well as the average propylene length (n_p) have been calculated by using the appropriate relationships between ¹³C NMR integrals, as reported in previous works.^[20,21] The results are listed in the supporting information (Table T1). Additionally, the comonomer reactivity ratio product ($r_p \cdot r_{C9}$), computed from the ¹³C NMR diad distribution^[22] is also shown.

Finally, the tacticity of propylene sequences was estimated from the methyl region (19.4–22.0 ppm) at the pentad level^[23]. The isotactic average length (n_I) was assessed from the relative contents of centred isotactic *mm* triads and *mx* triads, where x stands for any kind of isotactic sequence interruption, either C₉ insertion or both stereo (hetero *mr* triad) and regio misinsertion of propylene.^[24] The results are summarized in Table T2, provided in the supporting information.

The analysis of ¹H NMR spectra of samples revealed that different olefinic species were formed, as a consequence of several termination mechanisms of the chain growing process. In the case of PP homopolymers, vinylidene (4.71 and 4.78 ppm), vinylene (5.38–5.60 ppm) and isobutenyl (4.88–5.00 ppm) groups were detected. For C₉ copolymers, no isobutenyl groups were found but, together with vinylidene and vinylene species, allyl (two doublets: 4.97, 4.99, 5.02, 5.06 ppm) and tri-substituted (5.21 ppm) olefin groups appeared at variable ratios, depending on the C₉/propylene feeding ratio and T^{polymerisation}. The total content of double bonds was considered in order to estimate the molecular weight of samples, assuming that metallocene polymerisation yields only one terminal double bond every chain.^[17,19]

2.4. DSC characterisation: Melting temperature

The thermal properties were analysed in a TA Q100 Instrument calorimeter connected to a cooling system and calibrated with indium and zinc. The film samples were heated from -45 °C to either 160 °C for the C₉ copolymers or 180 °C for the PP samples, at a heating rate of 10 °C·min⁻¹. They were subsequently cooled at 10 °C·min⁻¹ down to -45°C and, finally, heated again up to 160° or 180 °C. The values of T_m were taken from the maximum of the endotherm peak obtained after the second heating scan. The results are shown in Table 1.

2.5. SEC characterisation: Average molecular weights and molecular weight distribution

The SEC analysis of the PP homopolymers was performed at 145°C in a Waters GPC/V 2000 equipment with refractive index and viscometer detectors. A set of three columns of the PL Gel type was used with 1,2,4-trichlorobenzene as solvent. The equipment was calibrated with narrow molecular mass distribution standards of polystyrene. The number average molecular weights are shown in Table 1 together with their corresponding polydispersity values.

2.6. FTIR characterisation: Chemical defects

The FTIR spectra of samples were recorded from the films, by performing 4 scans in a Perkin Elmer Spectrum Two, in the 4000-450 cm⁻¹ range, at a resolution of 2 cm⁻¹. The absorbance of the spectra was baseline corrected and normalised to the intensity of the 2722 cm⁻¹ peak. The oxidation degree of samples was tracked by means of the 1712 cm⁻¹ peak (carbonyl index-C.I.), which corresponds to saturated ketones and acids.^[25]

2.7. TGA characterisation: Thermal stability under nitrogen

TGA measurements were carried out in a Thermal Analysis TGAQ 500 device. The samples used were discs of 6 mm diameter and of approximately 5 mg cut from the film with a die. A heating ramp from 40 °C up to 600 °C at 2, 5, 10 and 20°C·min⁻¹ were used, under a 90 mL·min⁻¹ flow of nitrogen. The TGA curves obtained were used to calculate the apparent activation energy (hence forward referred as E_a) of the weight loss process, by using the isoconversional method proposed by Friedman ^[26]. The analysis of changes in E_a was mainly focused on the initial stages of the degradation.

3. RESULTS AND DISCUSSION

3.1. Molecular weight and thermal behaviour of C₉ copolymers

The presence of 1-nonene in the polymerisation medium affects drastically the molecular weight of macrochains. An important decrease of this magnitude is observed as the C₉ content increases, as shown in Figure 1. This drop with rising comonomer has been also noticed in other types of copolymers and terpolymers based on propylene and has been primarily ascribed in literature to the presence of transfer reactions^[20,27-30] as comonomer is incorporated. Molecular weight turns out also very much dependent on polymerisation temperature, as expected. Thus, the higher the $T^{\text{polymerisation}}$ is the lower the molecular weight attained becomes at a given comonomer amount. A noticeable feature can be, however, deduced: molecular weight diminishment is more significant at lower polymerisation temperature. Thus, molecular weight of the samples are rather different at low 1-nonene composition for the distinct series at specific C₉ content, while it becomes almost the same at the highest C₉ compositions. These synthesis conditions allowed preparing propylene rich copolymers (up to 12 mol % in C₉) with molecular weights ranging from around 39,000 to 6000 g·mol⁻¹ (see Table 1 and Figure 1).

Another evident characteristic derived from data in Table 1 is the variation of melting temperatures. Firstly, they show a clear decrease as the polymerization temperature increases. Moreover, there is also a decrease of melting temperature as content in C₉ is raised, for the different series synthesized at the several temperatures. These thermal features together with the just mentioned variation in molecular weight allow predicting larger chain mobility in the molten state, which is promoted by the presence of C₉ units. Such a change in the characteristic dynamics can be ascribed to weaker inter-chain interactions additionally to the achievement of main chain conformations, whose probability is absolutely beyond the reach in the more rigid PP sequences.^[31]

Figure 1. Variation of molecular weight with the C₉ content for the different series: (solid circles) ¹H NMR measurements; (open circles) SEC measurements.

3.2. Composition, regio and stereoregularity and chemical defects in C₉ copolymers

The ¹³C NMR analysis performed yields a practically identical distribution in composition, independently of the T^{polymerisation} value. Figure 2 shows the fit to a unique variation of the average propylene length (*n_p*) within the content range studied for all the

copolymers synthesised. The product of reactivity ratios of both comonomers, calculated by ^{13}C NMR, is found to be not far away from one in all series (Table T1 in the supporting information). Accordingly, the insertion of C_9 is always random and n_p is really representative of the mean value.

Figure 2. Dependence of the propylene average length (n_p : solid circles) and the meso average length (n_I : open circles) on the C_9 content for the different series. A colour code is inserted into the figure.

A clear different behaviour is, however, found for the stereoregularity of chains, as also shown in Figure 2, by means of the isotactic average length (n_I). Specific n_I trends are the consequence of tactic sequences distributions that depend on $T^{\text{polymerisation}}$. Figure 3 displays the results for the (*mmmm*) isotactic pentad in all the series. It is clearly noted the decrease observed in the population of this sequence for the iPP homopolymers, from 90 to 75 mol%, as $T^{\text{polymerisation}}$ increases from -5 to 60°C, what leads to the lowering of the melting temperatures. Simultaneously to this change in isotacticity, the content of hetero and syndio pentads rises. The complete data set is provided in the supporting information (Table T2).

Figure 3. Variation of the (*mmmm*) pentad content on C₉ content for the different series. A colour code is inserted into the figure.

The microstructure of metallocene PP is quite simple because of the absence of (*mrrm*), (*rrrr*) and (*mrrr*) pentads. As a matter of fact, the (*mrrm*) pentad is the sole interruption of isotactic sequences in the PP-5 sample and it coexists in the other PP samples with an increasingly content of (*mmrm*) and (*rmrr*) pentads, as $T^{\text{polymerisation}}$ increases (see Table T2 in the supporting information). This microstructure becomes even simpler when C₉ units are inserted. It is actually noticeable in Figure 4 that, just by insertion of around 2 mol% of comonomer at 10 °C, the isotactic (*mmmm*) pentads increase, the iso (*rmmr*) and hetero (*mmrr*) pentads decrease, and the hetero (*mmrm*+*rmrr*) and the syndio (*mrrm*) ones are hardly altered. At higher contents than 2 mol%, the relative amount of any of these sequences is almost constant. A similar behaviour is observed in any of the other copolymer series, as represented in Figures S1 to S3 in the supporting information. Such an unexpected microstructure variation reveals that the comonomer coordination with the active centre is, in

spite of the long chain associated with the double bond of the C₉ unit, easier than the one of a propylene unit entering by the wrong enantioface, thus producing a PP racemic diad.

Figure 4. Distribution of pentads in the copolymer series synthesised at 10°C. The identification of symbols is indicated into the figure.

Concerning regiodefects, their content is quite low (ca. about 0.5 mol%, as seen in Table 2 of supporting information) and no clear variation is detected as a whole with the C₉ insertion. Only some of the copolymers at the highest composition range lack of this kind of mis-insertions, indicating a more regioselective chain building when the comonomer is present.

Variation of n_I at every series is that commented in Figure 2, taking into account all kind of disruptions of isotactic selective propylene insertion, *i.e.*, the C₉ units, stereo and regio propylene mis-insertions. As expected from the influence of $T^{\text{polymerisation}}$ on tacticity, n_I is significantly shortened as polymerisation takes place at higher temperature for the iPP samples and the copolymers with low C₉ contents. Nevertheless, n_I becomes similar for the specimens with the highest C₉ amounts.

These variations in stereo-microstructure, together with the aforementioned molecular weight trends, are undoubtedly associated with the characteristic chain mobility in the molten state and are expected to play an important role in thermally activated chain scissions, implying that chain dynamics drives the energy required for such processes. Next, an attempt of proving this hypothesis will be developed.

The description of other abnormalities in composition is an essential point to be considered in order to find additional arguments. As commented, presence of oxygen containing groups and chain-end double bonds must be assessed as possible chemical defects affecting the thermal stability. Figure 5 displays the dependence of carbonyl index (C.I.), as deduced from the 1712 cm^{-1} absorbance, on comonomer content. An almost constant C.I. is found for all the samples at C_9 composition below about 5 mol%, whereas a slightly decreasing trend is observed beyond that content of 5 mol%. Two high C_9 content copolymers synthesised at $60\text{ }^{\circ}\text{C}$ do not fit that falling tendency, showing C.I. values particularly high.

Finally, presence of double bonds has been quantified by ^1H NMR. According to the commented mechanistic considerations, these groups are directly associated with the average molecular weight. Table 1 and Figure 1 display a good fit between values obtained for the molecular weights calculated from SEC and from ^1H NMR, for the iPP homopolymers, confirming that the olefinic structures considered are indeed chain-end placed. As indicated in the experimental section, the total content of end-chain double bonds has been taken into account without making a distinction between the different types. The important issue here is to get the knowledge on the content of anomalous groups that could be involved in the degradation since they might promote pure thermal scissions in the absence of oxygen.

Figure 5. Evolution of the carbonyl index (C.I.), as measured by the absorbance ratio between 1712 and 2722 cm^{-1} , on the C_9 content in the different series. A colour code is inserted into the figure.

3.3. Thermal stability under N_2

The insertion of C_9 as comonomer yields a deterioration of the anaerobic thermal resistance in the case of the copolymer series prepared at -5°C . Figures 6a and 6b clearly show a shifting toward the low-temperature side with the C_9 content for the TGA (Figure 6a) and DTGA (Figure 6b) curves obtained at $10^\circ\text{C}\cdot\text{min}^{-1}$. This behaviour is not exactly observed for the other copolymer series, synthesized at higher polymerization temperatures. Samples prepared at 10 and 25°C also display a shift down toward inferior temperatures but only at C_9 contents higher than 7 mol%. The weight loss seems to occur in the series synthesized at 60°C at temperatures lower than those presented by the -5 , 10 and 25°C series within a rather wide temperature range, without showing a clear trend with C_9 composition. TGA curves at $10^\circ\text{C}\cdot\text{min}^{-1}$ for these copolymer series can be checked in the supporting information (Figures S4 to S6).

Figure 6. a) TGA and b) DTGA curves obtained at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen for the copolymer series obtained at -5°C . Samples are identified by the colour code inserted into the figure.

The initial weight loss temperature (T_i) was taken as a criterion for comparing the stability. It was assessed as indicated in Figure 6a and it involves a relatively wide degradation interval (ca. about 20 wt%).^[9,16] Representation of T_i , measured from TGA

curves at $10^{\circ}\text{C}\cdot\text{min}^{-1}$, versus the C_9 content in Figure 7 illustrates the above remarks on evolution of TGA curves for each materials series. The series obtained at -5, 10 and 25°C exhibit a somewhat T_i depleting trend, similar to a homologous series based on copolymers of propylene with 1-pentene and 1-hexene.^[16] Moreover, the T_i values for these copolymers fall into the temperature range where the corresponding values for the 60°C series stay in. As already commented, T_i can be considered roughly constant at the 60°C series, if they are taken as a whole.

Figure 7. Dependence of the T_i of pyrolysis, obtained at $10^{\circ}\text{C}\cdot\text{min}^{-1}$, on C_9 content for the different series. A colour code is inserted into the figure.

The dependence of T_i on the C_9 content can be consistently justified keeping in mind that the temperature at which the weight loss starts varies with the number of chain scissions and the probability that these events yield volatile species. Both parameters are expected to increase with chain mobility^[32] and the reduction in molecular weight, *i.e.* when a rise of C_9 content and $T^{\text{polymerisation}}$ occur (see T_m and M_n values in Table 1). Accordingly, the T_i decrease

could not mandatorily be joined to decreasingly energy consuming scissions, as will be discussed later.

The estimation of the apparent E_a by means of the Friedman's multiple-heating rate approach^[26] reveals indeed a rise of the energy required for chain scission process, in the early stages, as it is shown in Figure 8 for series at -5 and 60°C and in Figure S7 for the other cases. It is apparent that the E_a build-up occurs into a conversion range that roughly extends up to roughly 20 wt. loss percentage and it eventually reaches similar plateau levels for all samples. Additionally, the detailed inspection of the rising stage reveals that E_a trends are significantly different for the two series. It is quite remarkable that samples of the CP series obtained at 60°C show higher E_a values at the initial stages of the degradation than those of the CP series at -5°C. Such E_a increment is also observed within each series when the C_9 content increases. The phenomenon can be better analysed in Figure 9, where specific E_a values at 2, 3 and 5 wt.loss% are represented as a function of the C_9 content, for all the series studied. The figures evidence that the energy required has some degree of correlation with C_9 content and it seems to be associated with $T^{\text{polymerisation}}$. In fact, the E_a increases with C_9 conversion at different levels, seemingly related with $T^{\text{polymerisation}}$. The perception of these changes is more apparent at 1 and 2 wt.loss%, but it can be still remarked at 5 wt.loss%.

Figure 8. Dependence of apparent E_a on the weight loss for CP series obtained at: a) -5°C and b) 60°C . Samples are identified into the figures through different line styles

Figure 9. Dependence of apparent E_a , measured at 2, 3 and 5 wt.loss%, on C_9 content for the pyrolysis of the different series. A colour code is inserted into the figure.

At this point of the study, it is worth checking the correlation between E_a and the factors that have been claimed to be responsible for the initial low E_a processes. The first one is the existence of oxidation traces in the samples. Its influence can be inferred from Figure 10, which shows the E_a values obtained for low conversion stages (2, 3 and 5 wt.loss%) versus the carbonyl index. The graphs depict a lack of relationship between the E_a and the oxidation level of samples, since most of them are located within a narrow C.I. range (ca. between 0.070 and 0.095) and they show E_a values over the whole interval measured.

The second factor is the presence of end-chain double bonds. In this case, the evidence about the non-determining role of these groups comes from the fact that the E_a required for chains to break rises, despite the increasing content of these species with both $T^{\text{polymerisation}}$ and C_9 insertion.

Figure 10. Independence of the apparent E_a and the carbonyl index, at the weight loss indicated, for the different series. A colour code is inserted into the figure.

It is important to emphasize that C₉ insertion implies a sharp decrease of T_m, which greatly reduces viscosity of the molten state and allows radicals diffusing faster, thus promoting a larger number of scissions. In this sense, an earlier weight loss could be accounted for, as long as C₉ content grows up, but the E_a increase could not be explained. This E_a trend is definitely associated with the involvement of other chain structures in the most energy demanding step of the process, *i.e.* in the main chain breakage. As previously shown, the metallocene synthesis yields both shorter and less isotactic chains when T^{polymerisation} rises from -5 to 60°C. Consequently, the energy consumption in the pyrolysis of these samples must be correlated to changes induced by these two microstructure features in chain dynamics, which is eventually the parameter driving the resistance to thermal main chain C-C cleavage in the molten state.

Among the different microstructure parameters, the propylene sequence length is really identical in all the copolymer series because of the random insertion of the C₉ units (Figure 2). Therefore, differences in the distribution of composition can be discarded as a factor determining the characteristic E_a of pyrolysis. On the contrary, microstructure in configuration was found to depend on T^{polymerisation}. Actually, it was shown (Figure 2) that the isotactic average length is highly dependent on T^{polymerisation}. As expected, the lower T^{polymerisation} is the longer *n_I* becomes and the largest differences are found at the lowest C₉ content. Accordingly, *n_I* is a parameter that could play a decisive role in thermal breaking of chains. In fact, the correlation of this microstructure feature with the apparent E_a at low weight losses is straightforward for the entire range covered by the samples. It is clear from Figure 11 that E_a values at 2, 3 and 5 wt.loss% can be fitted into two linear relationships, intersecting at *n_I* values around 15 units. Such a change in the E_a variation reveals that there must be other T^{polymerisation} dependent parameter playing also an important role. On the basis of

our previous work^[14] and the simulation from a theoretical model,^[32] that factor is proposed to be the molecular weight.

Figure 11. Variation of apparent E_a of pyrolysis with the isotactic average length, at the weight loss indicated, for the different series. A colour code is inserted into the figure.

The E_a of the initial pyrolysis stage for a high molecular weight iPP was shown to be quite low,^[12,14] suggesting that chain size must play a significant role from a minimum value, able to affect remarkably chain dynamics. The representation of the E_a in the early stages of the pyrolysis, for the C₉ copolymers, as function of the molecular weight in Figure 12 unravels rather similar trends to those obtained with n_I (Figure 11). The E_a trend comprises two linear ranges intersecting at a molecular weight around 20000 dalton. At higher values, the initial E_a of the pyrolysis tends to the limit value found for high molecular weight specimens (ca. 100 KJ.mol⁻¹).^[9,12,14,33] It can be then proposed that there exists a molecular weight threshold above which, restrictions in chain dynamics caused specifically by the high length of chains,

both intra-chain interactions and inter-chain entanglements, justify the existence of local structures where mechanical tension is concentrated, behaving as weak points. At M_n lower than around 20000 dalton, the initial E_a would be more dependent on the isotactic average length rather than on chain size itself, because of the reduction of chain entanglement.

Figure 12. Variation of apparent E_a of pyrolysis with the molecular weight, at the weight loss indicated, for the different series. A colour code is inserted into the figure.

4. CONCLUSIONS

Several series of isotactic PP and poly(propylene-*co*-1-nonene) copolymers, up to 12 mol% in comonomer content, have been synthesised at different polymerisation temperatures, resulting on samples in a wide molecular weight range as well as with different average lengths in both propylene and meso units.

The thermal stability under anaerobic conditions of the homo and copolymers is found to be dependent on structural features that determine chain mobility. In particular, the molecular weight and the isotactic average length. Whilst the apparent E_a of initial chain scissions is rather low (ca. 100-130 KJ·mol⁻¹) for molecular weights above roughly 20000 dalton, the energy required for such a process is increased up to reach values around 225 KJ·mol⁻¹ below that molecular weight, when propylene isotactic sequences are very short (ca. under 15 units).

High molecular weights and long propylene isotactic sequences are thought to promote specific intra and inter-chain interactions, which play as weak points under thermal stress. Diminution of both molecular weight and isotactic average length entails the concurrent increase of the chain mobility and the energy required to produce initial chain breakages.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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