



Use of SSA to detect structural changes in metallocenic ethylene/ α -olefin copolymers and their free radical post-reactor modifications



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ABSTRACT

The successive self nucleation and annealing (SSA) methodology has been shown to be successful to characterize the lamellae structure of many polyolefins. The differences in molecular structure of metallocenic α -olefin copolymers with varied comonomer type and content were characterized by this technique with a conventional DSC. This thermo-structural characterization process was also applied to analyze the changes induced on a 1-octadecene - ethylene copolymer modified with different post-reactor methods: several doses of gamma-radiation, peroxide modification and oxidative degradation. These modifications induced crosslinking and branching on the original copolymer affecting its molecular weight and the crystalline structure. The SSA technique revealed detailed changes in the lamellae formation of the materials obtained as a consequence of the different methods of modification employed in this work. Mainly, crosslinking and branching sites restrained the mobility and length of CH₂ sequences to form lamellae, while degradation led to preferential chain scission at branched carbons making easier the formation of higher melting temperature lamellae.

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1. Introduction

The solid state properties of linear polyethylenes can be modified by copolymerization of ethylene with α -olefins of diverse chain lengths in different concentrations. Employing metallocenic catalysts, a broad range of polyethylenes can be obtained in this way [1]. However, for some specific applications, the ample variety of materials obtained by synthetic procedures must follow a post-reactor procedure in order to further modify their properties (e.g. enhance mechanical or processing properties). Irradiation, degradation or chemical modifications are some examples of common methods to induce changes in the structure of a given polymer. All these reactions alter the molecular structure of the polymers by inducing the formation of macroradicals on the polymer chains that can react with other radicals, antioxidants, oxygen or other macromolecules, leading to different cleavage or crosslinking reactions [2–11]. The relative rates of these reactions depend mainly on the concentration of free radicals, the presence of oxygen and the type

of carbon substitution. As an example, if the modification is performed by low dose rate of radiation in the solid state, most of the reaction occurs on tertiary carbons [2]. Also, crosslinking and branching effects are predominant in absence of oxygen, while chain scission reactions prevail in its presence [2–6].

Standard Differential Scanning Calorimetry (DSC) techniques do not allow the appreciation of some of the subtle structural changes involved in a number of the post reactor modification techniques mentioned above. Especially when they involve modifications that comprise about 0.1% of the carbons present [3]. However, the cleavage reactions in tertiary carbons lead to important structural changes that can be recognized and quantified by the Nucleation technique in successive self nucleation and annealing (SSA) [2,3]. The SSA technique has been developed to characterize structures of semi crystalline polymers which can generate crystals of different thicknesses from the molten material [12–14]. It is based on sequential implementation of self-nucleation and annealing steps in the sample, with decreasing temperatures. After this thermal conditioning, a final heating test reveals different melting peaks corresponding to the crystalline lamellae populations with different lamellar thicknesses that are generated during the stage of self-nucleation and annealing. In this way, this method can

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differentiate crystallizable segments of different lengths, associated with differences in frequency of chain branching. This is based on the relationship between the crystallization temperature and the length of the crystallizable segments between successive branch points generated during modification of the polymer. A conventional DSC can be used in this way for the heat treatment of the samples providing similar results to those obtained by Temperature Rising Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF). The SSA technique offers the additional advantage that the same type of experiment can be used to study semi crystalline polymers with some degree of crosslinking.

The SSA technique can be considered as a selective fractionation of crystallizable lengths of polymethylene sequences lengths, because the higher temperature annealing steps are intended to allow time for diffusion and growth of lamellae to an equilibrium value. Being the thicker lamellae formed first during the higher temperature annealing stages, we can expect that the diffusion processes that contribute to forming thinner lamellae will be increasingly restricted as the crystallization temperatures are reduced, and therefore most useful information will be obtained from changes in the thicker lamellae populations. Thicker lamellae, which form at the highest annealing temperature, will reflect more faithfully the changes in molecular structure; thinner lamellae may not reach an equilibrium state, and some structural changes may be masked because of this fact [15,16]. Because of these reasons, the final lamellae population distribution will depend on the annealing steps distribution chosen.

In order to follow up the different crystallization behavior in semicrystalline polyethylene structures through SSA, two 1-hexene and one 1-octadecene metallocenic copolymers of ethylene were studied. In addition, the relation between lamellae formation and the structural changes occurring as a consequence of various post-reactor processes was analyzed for the 1-octadecene – ethylene copolymer. Mainly, the effects of gamma irradiation, peroxide reaction and oxidative degradation were analyzed. The polymers and their modified samples were also analyzed by sol–gel extractions and gel permeation chromatography (GPC) in order to obtain information of the changes in molecular weight distribution.

2. Experimental

2.1. Materials and samples preparation

Ethylene-hexene (EHC) and ethylene-octadecene (EOC) copolymers were synthesized using a 1-L Parr reactor with stirring (500 rpm) at 60 °C with an ethylene pressure of 2 bar. The catalyst/cocatalyst used was Et(Ind)₂ZrCl₂/MAO. The reaction was carried in toluene solution for 30 min and stopped with methanol acidified with HCl (2%). The resulting polymers were precipitated and then washed with methanol and acetone. Finally, the product was dried at room temperature. ¹³C-NMR was used to determine their comonomer content [1].

2.2. Oxidative degradation procedure

About 7 g of each copolymer were placed in test tubes in an oven at 90 °C for 15 days in air. Samples of these copolymers were taken at 1, 3, 10 and 15 days to evaluate the changes occurring at different exposure times.

2.3. Peroxide modification procedure

2,5-dimethyl-2,5-di (tert-butyl peroxy)-hexane (DBPH) (Akzo Chemical of Argentina) was used as the peroxide initiator for the modification process. Fractions of fine powders of the synthesized

copolymers were impregnated with different amounts of peroxide–hexane 0.5% w/v solution to give the desired final peroxide concentrations once the solvent was removed. The quantities of peroxide added to each copolymer ranged from 800 to 4700 ppm. The impregnated polyethylenes were placed between 3-mm-thick steel plates held apart by a 0.5-mm-thick brass frame. The samples were then compression molded between the hot plates of a hydraulic press for 15 min at 170 °C and 10 bar. Then the pressure was relieved and the samples were kept at 170 °C between the plates for another 15 min. The reaction time and temperature were chosen on the basis of previous rheological experiments that allow determining that in these conditions full reaction of the DBPH peroxide was accomplished [7,17,18].

2.4. Irradiation procedure

Films of the different copolymers were prepared by compression molding for 2 min at 180 °C and 10 bar using the same hydraulic press. The films were inserted into Pyrex tubes, attached to a vacuum glass line and left under high vacuum for 24 h. The samples were then sealed in those same tubes and exposed at room temperature to different doses of γ -rays generated by a ⁶⁰Co source. The applied doses range from 29 to 138 kGy, using a dose rate of 8 kGy/h. They were measured with a Red Perspex dosimeter. The error in dose is estimated to be in the order of 5%. Following irradiation, the polymer samples were annealed for 2 h at 140 °C to assure undetectable levels of long-living radicals [19].

2.5. Characterization

2.5.1. Sol–gel analysis

Sol–gel analysis was performed to determine the insoluble gel fraction obtained in the copolymer following irradiation with different doses. For this purpose, irradiated samples were weighted, packed in paper filters and placed inside round bottom flasks containing xylene. The flasks were then immersed in an oil bath at 130 °C and the samples were extracted five times for 24 h renewing the solvent after each extraction. About 0.5 wt% Irganox 1010 was added and nitrogen was bubbled continuously during the extractions to avoid oxidation of the samples. After the extraction cycle was completed, the fraction of polymer solubilized in the solvent was precipitated and washed with cold methanol and vacuum dried to a constant weight. The remaining insoluble part was also washed and dried in similar manner.

2.5.2. Size exclusion chromatography (SEC)

The molecular weight of the materials was determined by size exclusion chromatography in a Waters 150C ALC/GPC equipped with three PLgel Mixed-A 300 × 7.5 mm², 20 mm pore size, columns (Polymer Laboratories). Two detectors were used, a refractive index detector—RI (Waters) and a multi-angle laser light scattering MALLS (Dawn DSP, Wyatt Technology Corporation), working at a wavelength of 690 nm with a dn/dc = −0.091 ml/g for polyethylene samples [8]. The analyses were performed at 135 °C with a 1,2,4-trichloro benzene flow rate of 1.0 ml/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene (Pressure chemical) and polyethylene (NIST).

2.5.3. Evaluation of basic thermal behavior

Whole (not extracted) samples were used throughout for all the DSC characterization and SSA experiments. Small disc samples (approximately 10 mg) were cut from films of all original and modified materials. The samples were encapsulated in DSC aluminum pans. Ultra high purity dry nitrogen was used as an inert atmosphere for conditioning and testing the samples in a Perkin

Elmer Pyris I calorimeter. A first characterization of the thermal behavior of the polymers was performed on the DSC by cooling and heating runs between 0 and 115 °C at a heating rate of 10 °C/min. To erase all previous thermal history, all samples were previously held in the molten state at 150 °C for 5 min.

2.5.4. SSA technique

The SSA technique consists of successive heating and cooling cycles. The self-nucleation and annealing temperatures (T_s) were chosen according to a regime defined by Fillon et al. [20]. Samples were first heated and held at 150 °C for 5 min to give an initial standard thermal history. Afterwards, they were cooled down to room temperature at 10 °C/min. Another heating scan followed, at the same rate, to a selected self-seeding temperature denoted T_s . The sample was then kept for 5 min at that temperature before cooling it again down at the same rate. The first applied T_s is chosen so that the polymer will only self-nucleate (i.e. T_s should be high enough to melt all the crystalline regions, except for small crystals fragments and/or nuclei that can later self-seed the polymer during cooling, e.g. 100 °C for EOC7). After that, the samples were heated once again up to a temperature 3 °C below T_s and held for 5 min. The crystals not melted at this temperature would anneal and some of the molten species would isothermally crystallize at this new temperature. The remaining molten crystallizable chains would only crystallize during the subsequent cooling. This cyclic procedure was repeated by heating the sample at a temperature 3 °C lower than that of the previous annealing, until a heating temperature close to 70 or 40 °C was reached, depending on copolymer. Melting patterns of the samples thus prepared were recorded at a heating rate of 10 °C/min. The final heating scan after this thermal fractionation reveals a series of multiple melting peaks that are a reflection of the multiple lamellar thicknesses obtained [13–15].

The first and last applied T_s depend on copolymer assayed. For example, by modified and original EOC7, the first T_s was 112 °C (the melt of EOC7 ends in 100 °C) and the last T_s was 82 °C. In the case of EH9 and EH16, the initial and final applied T_s were 100–70 °C and 72–42 °C respectively.

The same experimental procedure was used for all samples.

3. Results and discussion

3.1. SSA for 1-olefin/ethylene copolymers

Table 1 details the different copolymers studied in this work. The thermal properties reported there were obtained by commonly controlled cycles of heating and cooling through DSC. The different copolymers exhibit low crystallinity levels depending on the monomer type and content. Values for the average lengths for polymethylene sequences were calculated from comonomer concentrations. Estimations for the longer crystallizable polymethylene sequences were calculated from SSA higher temperature peaks, as discussed below. The almost constant ratio for these two values suggests similar copolymerization statistics for copolymers EOC7 and EHC9. Fig. 1 shows the wide melting thermograms obtained for these semicrystalline polymers, already discussed in previous works [7–9].

Fig. 2 displays the final melting runs after applying the SSA technique to these copolymers. This figure also provides the same information but expressing temperature in terms of polymethylene sequence length, in the upper x axis. This allows a better visualization of how the longer polymethylene sequences changes affect the thermal behavior [21] by associating each peak melting temperature with a polymethylene sequence length expressed in terms of number of carbon atoms. In order to perform this association, a regression through published results of the melting temperature of

n-alkanes as a function of the chain length leads to the following relationship [18]:

$$n = 12.98 + 1.71 \exp\left(\frac{T_m}{29.53}\right) \quad (1)$$

Here n is the number of C atoms in the sequence, and T_m is the peak melting temperature (°C).

The applied SSA treatment allows separation of between nine to eleven populations of lamellae in the same thickness range for each sample. The different DSC peaks correspond to the melting of crystallites with dissimilar average thickness. Higher melting temperatures correspond to lamellae of larger thickness values.

The melting peaks obtained after the SSA treatment reflect narrow distributions of lamellae thicknesses that depend on the available crystallizable polymethylene lengths, and also on the set of chosen T_s temperatures. As the single DSC thermograms for EHC9 and EOC7 shown in Fig. 1 are within a similar temperature range, the chosen T_s set was kept to be almost the same for both copolymers. This allowed studying the true evolution of amounts of particular crystallizable polymethylene sequences within these two copolymers containing similar concentrations of comonomers of different chain length. As EHC16 has a different thermomorphological behavior, the selected T_s set was one more suitable to the temperature range covered by the single thermogram shown in Fig. 1. The different melting temperatures between EHC9 and EHC16 make it difficult to contrast them by SSA.

EHC9 and EOC7 copolymers have as comonomers α -olefins with different chain length and similar concentrations. DSC results show comparable overall crystallinity as observed in Table 1. This fact suggests similar copolymerization statistics. However, the SSA technique shows that the width of the area distribution for peaks corresponding to lamellae with larger methylene sequences found for the EOC7, is significantly higher than for the EHC9. The SSA–DSC endotherm areas are proportional to the mass fractions of crystalline phase that are formed at each self-seeding temperature T_s . These differences in SSA results are originated in the fact that the EOC7 copolymer has a branching concentration almost 25% smaller than the EHC9 copolymer. This lead to a longer average sequence of methylenes between branches that can form larger lamellae in the EOC copolymer.

3.2. SSA for modified copolymers

The synthesized EOC7 copolymer was subsequently modified by different post-reactor processes that led mainly to crosslinking reactions: vacuum gamma irradiation in the solid state and peroxide reaction in the melt. As the level of crosslinking increases, the reaction reaches a point where there is at least an average of one crosslink per polymer chain. Beyond this point part of the polymer mass turns into an insoluble gel. This transition is known as the Gel Point, and the dose of radiation or peroxide needed to reach this condition is termed the Gel Dose (Dgel). Samples beyond the Dgel are known as post-gel samples, and present some insoluble gel content (Tables 2 and 3). These changes in the structure directly affect the thermo-morphological behavior of modified EOC7 samples.

Tables 2 and 3 show the results of conventional DSC runs for irradiated and peroxide modified samples respectively. Increasing the radiation dose or the peroxide concentration caused a slight reduction in the crystallization and melting temperatures, and in the percent of crystallinity (X_c). This is due to the insertion of more branching points induced by the crosslinking reactions. When SSA is applied to analyze the thermal behavior of the irradiated or peroxide modified post gel samples it is clear that, as the radiation

Table 1
Thermal and structural properties of the copolymers used.

Copolymer	%Molar incorporated monomer	AvN ^a	LLPS ^b	Xc (%)	Mw (Da)	PD	Dgel (ppm DBPH)	Dgel (kGy)
EOC7	7.1	26.3	62	31	98,700	1.76	2730	36
EHC9	9.2	19.7	53	28	86,400	2.10	2610	36
EHC16	16.1	11.5	33	19	73,300	2.01	nd	62

nd: not done.

^a Number average length of CH₂ sequence.

^b Length of the longer polymethylene sequence (LLPS) detected by SSA.

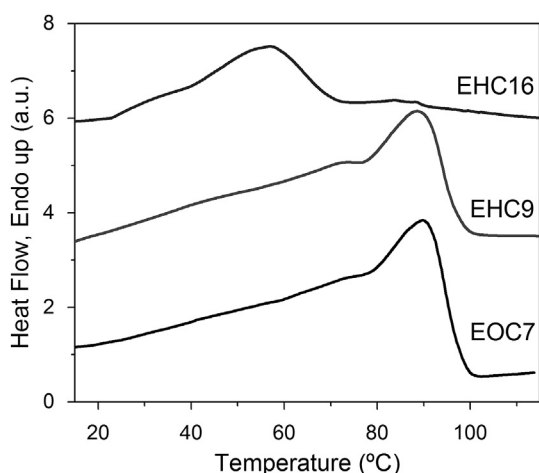


Fig. 1. DSC heating scans at 10 °C/min for the original copolymers.

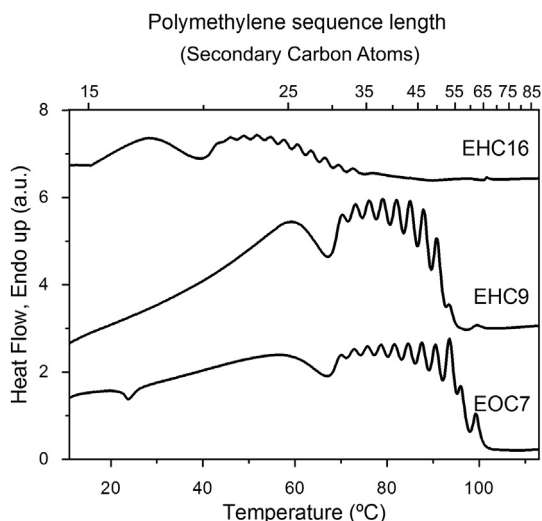


Fig. 2. SSA thermograms at 10 °C/min of the original copolymers as a function of temperature and of the polymethylene sequence length.

dose or peroxide concentration increases, there is an inhibition in the formation of lamellae with larger polymethylene sequence lengths. The formation of lamellae with greater thickness is reduced by the contribution of two factors: the first one is the reduction of the population of crystallizable blocks available in the copolymer at its larger end, which is statistically the most favored by crosslinking reactions. The other factor is the raise of topological constraints due to crosslinking that affect the diffusion processes of short range [2,3].

However, this effect in thicker lamellae is more accentuated in

the peroxide modified samples. It can be clearly seen that samples near the Dgel, at 2800 ppm, are more affected than the ones irradiated with doses well beyond Dgel. Comparison of the results shown in Figs. 3 and 4, corresponding to irradiation and peroxide modification shows that similar DSC-SSA response is obtained by irradiation with 135 kGy, that is almost 4 times the Dgel and with 4700 ppm of DBPH that is about twice of Dgel for peroxide modification.

Taking into account what was explained above; this behavior may be attributed to a different way of crosslinking. As it was discussed in a previous work on this copolymer [7], at similar dose distances from Dgel the copolymer showed a higher gel content with peroxide modified samples. For example, in this work we report the SSA analyzes of EOC7 at 89 kGy which has 77% gel content, and EOC7 at 4700 ppm which has 82%. In that other study, the higher gel content was attributed to a higher reaction rate for vinyl ended-polymer chains with secondary polymer radicals (vinyl decay was larger for the peroxide modification than for irradiation at similar advances of reaction). Such type of reactions should go easier in the peroxide modification as it is done in the melt state, giving the chains and radicals more mobility and thus, more probability to react [7]. As a consequence, each repetitive unit has much more probability to react, while in the irradiation process, the repetitive units allocated in the crystalline phase are restrained and not so prone for reaction with radicals. Therefore is logical that the peroxide modified samples near the Dgel (4700 ppm) have less high temperature lamellae formations than the irradiated post-gel samples.

On the other hand, some scission could be expected from tertiary carbons, or oxygen present in the atmosphere during polymer modification. However, gamma irradiation was conducted in vacuum without any easily observable degree of scission, meaning that tertiary carbon concentration is not enough. Even the peroxide modification didn't present any observable scission. On the contrary, as it was discussed, chain branching because of accelerated crosslinking reactions through vinyl ended chains was favored. These observations are explained in detail with SEC and rheological experiments [7].

3.3. SSA for degraded copolymers

Samples of EOC7 were degraded at 90 °C in air during 15 days. Table 4 and Fig. 5 show changes in thermal properties and molecular weight suffered by the EOC7 copolymer at increasing exposure

Table 2
Properties of EOC7 modified with gamma irradiation.

EOC7	x (%)	Mw (g/mol)	Gel (%)	Tc (°C)	Tm (°C)
Original	31	98,700	–	72.1	89.8
20 kGy	28	158,700	–	71.4	89.5
89 kGy	26	Nd	77	67.2	85.1
135 kGy	nd	Nd	90	66.0	83.5

Table 3
Properties of EOC7 modified with organic peroxide.

EOC7	Xc (%)	Mw (g/mol)	Gel (%)	Tc (°C)	Tm (°C)
Original	31	98,700	–	72.1	89.8
800 ppm	29	124,100	–	67.7	89.4
2800 ppm	28	537,400	6	59.1	82.1
4700 ppm	26	nd	82	57.5	81.2

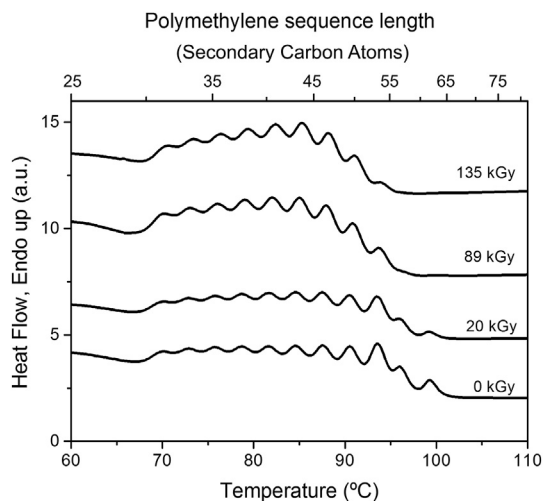


Fig. 3. Thermograms at 10 °C/min of irradiated EOC7 as a function of temperature and of the polymethylene sequence length. Dgel = 36 kGy.

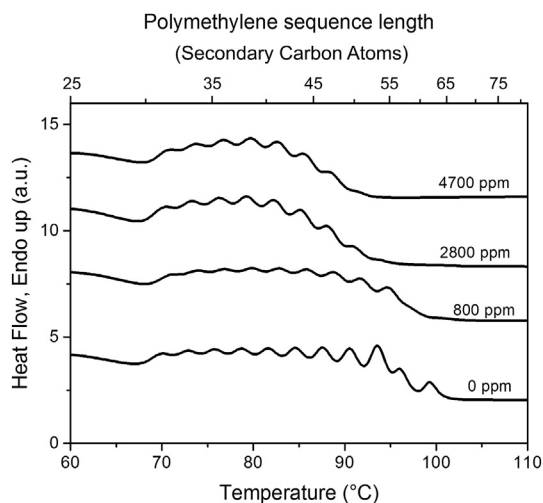


Fig. 4. Thermograms at 10 °C/min of DBPH modified EOC7 as a function of temperature and of the polymethylene sequence length. Dgel = 2730 ppm DBPH.

times inside the environmental chamber. The alterations on thermal behavior are opposite to those observed with irradiation or peroxide modification. Thermal degradation leads mainly to scission of chains, and thus, a decrease in the average molecular weight as it is observed in Fig. 5 the SSA technique shows the emergence of melting peaks corresponding to thicker lamellae in Fig. 6 [16]. As tertiary carbons are more prone to scission reactions [2,3,10], a selective attack on tertiary carbons can eliminate the disruption of crystalline sequences due to short chain branching, allowing methylene units neighboring tertiary carbon atoms to crystallize [2,3]. Then, there is a higher amount of polymethylene sequences

Table 4
Properties of EOC7 aged in air.

EOC7	Xc (%)	Tc (°C)	Tm (°C)
Original	31	72.1	89.8
1 day	35	70.0	88.8
3 days	36	71.4	89.3
10 days	38	72.0	90.7
15 days	38	72.3	91.3

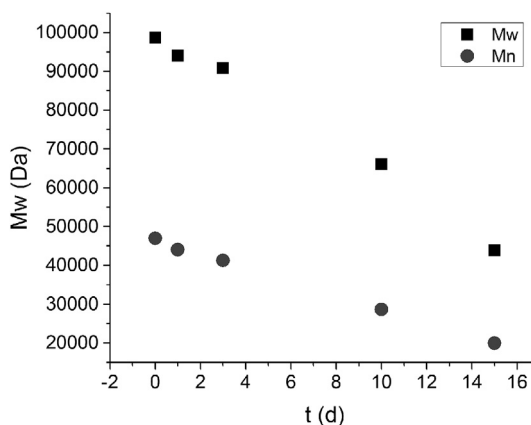


Fig. 5. Effect of the thermal degradation in oxygen over EOC7 molecular weights.

available which increase the thickness of the lamellae that can form in the higher stages of crystallization temperature [16].

4. Conclusions

The SSA technique results give information on the changes of longer polymethylene crystallizable lengths. Metallocenic synthesis provides polyolefins with the desired concentration and length of side chain branches into statistical linear ethylene- α -olefin copolymers, using variable concentrations of the comonomer. In this work, SSA was firstly applied in two 1-hexene – ethylene copolymers with significantly different comonomer contents. Even the most amorphous copolymer (around 19%, DSC single characterization) could show some lamellae formation, although difficult to quantify individual lamellae size fractions. The other

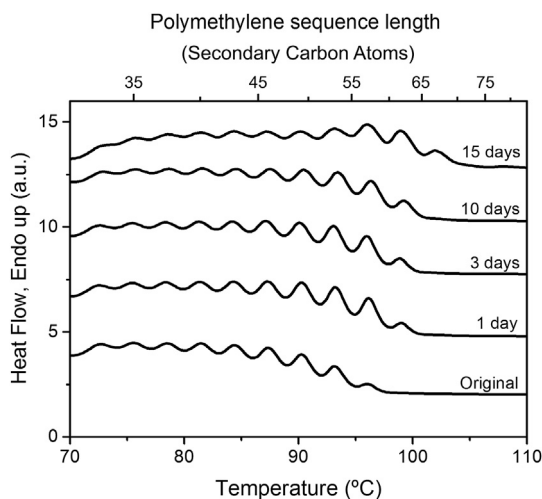


Fig. 6. Thermograms at 10 °C/min of EOC7 original and aged in air as a function of temperature and of the polymethylene sequence length.

semicrystalline ethylene-hexene copolymer was compared to a 1-octadecene – ethylene copolymer having similar crystallinity (around 30% crystallinity by DSC). SSA showed that the EOC7 copolymer presented lamellae with longer polymethylene crystallizable sequences, due to the lower short branches concentration.

SSA was used also to analyze the structural changes of post-reactor procedures involving radical reactions of crosslinking and scission. Samples of EOC7 were submitted to vacuum gamma-irradiation and peroxide (DBPH) modifications. These processes increase the molecular weight of the polymer mostly by crosslinking reactions between radicals. Comparing both procedures, these effects were more accentuated in the DBPH modified samples at similar advances of reaction. That could be due to higher probability of chain branching and crosslinking reactions due to unconstrained sequences in the melt.

On the other side, samples of EOC7 were degraded at 90 °C in presence of oxygen, leading to thermal degradation as a function of time. This effect was observed by average molecular weight decrease by chain scission reactions in tertiary carbons due to radical attack. As tertiary carbon atoms were preferentially degraded, longer polymethylene sequences were allowed to form thicker lamellae for the most degraded samples. That was observed through SSA, as higher melting temperature endotherms appeared in degraded samples.

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