

SSA study of early polyethylenes degradation stages. Effects of attack rate, of average branch length, and of backbone polymethylene sequences length distributions

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ABSTRACT

Low-density polyethylenes have been attacked by free radicals in the presence of oxygen to promote chains scission, aiming at showing effects of the molecular structure on the thermal behavior as determined by using a Successive Self-Nucleation and Annealing (SSA) technique. Three types of low-density polyethylenes were used: a hydrogenated polybutadiene (HPB), as a model for a statistical linear ethylene–butene copolymer, a linear ethylene–butene copolymer (LLDPE) with short branches not randomly distributed along the main chains, and a low-density polyethylene (LDPE) with randomly placed long and short branching. All the polymers were subjected to thermal oxidation in air. Additionally, the LDPE and HPB were exposed to gamma irradiation in air, while the HPB was also degraded with an organic peroxide. By virtue of the thermally activated oxidation, the three polymers show signs of molecular scission evidenced by the appearance of endotherms in the high temperature range of the final SSA thermogram. These endotherms are associated with the melting of thicker crystals formed by longer polymethylene sequences that were not available for crystallization in the original polymer. Similar indication of chain scission was detected in some of the irradiated HPB. In the case of the irradiated LDPE or the HPB modified with peroxide, the main effect observed was crosslinking that was identified by a reduction of the area of the higher melting endotherms in the final SSA thermogram.

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1. Introduction

The properties of many semicrystalline polymers are routinely modified by molecular structural changes caused by attack of free radicals. Free radicals formed on the main chain atoms set off a variety of reactions that end at modifying the molecular macrostructure. The free radicals can be provided by oxygen at sufficiently high temperature, peroxides decomposition, or high energy radiation [1–3]. The above mentioned methods can give increasing rates for free radicals formation. Lower attack rates, linked to lower concentrations of free radicals, are expected to be more selective for reaction with tertiary carbon atoms, owing to differences in the chemical reactivity between tertiary and secondary carbon–hydrogen bonds.

Oxygen diffuses faster into amorphous polyethylene regions of the solid polymer, as compared with diffusion into crystalline regions, and therefore it is expected to react first with sections of the molecules placed at this amorphous phase [4]. It has been shown that sample thickness has to have an important influence on oxygen attack for these polyolefins, as expected [5–7]. Furthermore, the amorphous phase is much richer in branching points than the average molecule, and therefore we could anticipate a preferential attack on tertiary carbon atoms. Some copolymers of ethylene with propylene may be found not to follow this rule, as the methylene side groups are small enough to be included as defects in the crystals when significant cooling rates are used for the melt crystallization [8,9]. At decomposition temperature, peroxides will be finely dispersed in the molten polymer, where no preferential transport velocity zones exist in the liquid, and we can safely assume that the free radicals thus obtained will be evenly distributed into a homogeneous phase with average branching points concentration. Free radicals generated by high energy irradiation processes are at first homogeneously distributed, regardless of the

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physical state of the polymer – either liquid or semicrystalline – but the reactions paths following this initial step depend strongly on the media mobility. Free radicals located at the high-mobility amorphous or liquid regions will react relatively fast, mainly by reaction with other radicals, with antioxidants, with oxygen or with other macromolecules. Some free radicals are located in the crystalline phase, and will react at a much slower rate [4,10].

Reactions of free radicals with macromolecules main chain atoms may produce chain scissions or crosslinking, depending mainly on whether the reacted carbon is a secondary or a tertiary one. Secondary carbons produce much more crosslinking than tertiary ones. Reactions in the melt state produce more homogeneous molecular structural changes. Reactions in the solid state will produce in some cases – like medium and low-density polyethylenes – most changes for the sectors of the molecules located in the amorphous regions that include a tertiary carbon atoms concentration higher than the average.

To precisely model the polymer molecular structure changes caused by these processes, quantitative measurements of molecular structure evolution are needed. Besides quantitative measurement of reaction extent, that is very useful for homopolymers, the precise placement of chains scission events (either secondary or tertiary carbons) is very desirable for detailed modeling. As mentioned in an earlier article [7], initial stages of the structure evolution are the most difficult to detect and quantify. Size exclusion Chromatography can be useful for homopolymers structure evolution, but small changes can be detected and quantified only when model polymers are used as starting material. Spectroscopic methods are often not sensitive enough to detect carbon reactions extents in the order of 10^{-4} M. Other methods like Temperature Rising Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF), give information only on changes of average crystallizable sequences lengths. More detailed information on chains scission at tertiary carbon atoms can be obtained via a technique that may look at changes of crystallizable sequences lengths, like Successive Self-Nucleation and Annealing (SSA) [7].

The SSA technique [7,11,12] can be considered as a selective fractionation of crystallizable lengths of polymethylene sequences lengths. After erasing all previous thermal history in the samples by heating and keeping them well above the melting temperature, the polymer is allowed to anneal in successive stages at lower temperatures, to promote growth of the thicker stable lamellae. The annealing steps allow time for diffusion of chains along their contour for best lamellae growth (annealing stage). A final heating run reveals the melting of the lamellae thickness populations induced by the previous treatment. For analysis, in this work special attention is centered at the higher temperature melting peaks that correspond to thicker lamellae, as explained below in the discussion. As these grow without any other diffusion restriction than liquid topology, they reflect more faithfully details of the true upper end of the distribution of crystallizable polymethylene sequences lengths in the liquid state. Lamellae grown at lower annealing temperatures are formed from chains that have more restricted diffusion and folding movements, and might not reach their full thickness and extent. Also another type of graph is proposed to be used for SSA analysis, where the temperature abscissa is transformed into polymethylene sequences length values, for easier viewing of the molecular structure changes.

For some branched polyethylenes, free radicals attack in conditions that produce chains scission have been linked to the formation of SSA melting peaks at temperatures higher than the highest observed for the unreacted polymer [7,12]. These higher temperature peaks have been shown to correspond to longer crystallizable polymethylene sequences lengths that were not available for lamellae formation in the unreacted polymer. As the

higher temperature melting peaks are formed from liquid only, as mentioned above, it was concluded that the only restriction ought to consist of chain defects like branching points. The origin of these polymethylene sequences is thus linked to the chains scission at tertiary carbon atoms [7,12]. Details as the mass fractions corresponding to these higher melt temperature lamellae, and the variable melting temperature shift from the original SSA spectra have not been analyzed in the literature.

Here we compare experimental results obtained for several branched polyethylenes to show the effects of: a) the selectivity of the free radicals attack, b) the branches length distribution, and c) intermolecular polymethylene sequences length distributions, on the SSA highest melting temperature and amount of crystals involved in it. Free radicals used for the chemical attack have been supplied by oxygen, by peroxides decomposition, and by high energy irradiation, to explore the effects of increasing free radicals concentrations.

Three types of low-density polyethylenes have been attacked by free radicals in the presence of oxygen – that promotes chains scission – to show effects of molecular structure on the final SSA spectra. Hydrogenated Polybutadiene (HPB) is here used as a model linear polyethylene with statistically distributed short branching and homogeneous intra- and intermolecular chemical composition distributions. HPBs have also been well established as model copolymers with very narrow molecular weight and chemical composition distributions [13]. Low-density polyethylene (LDPE) is here used as a typical polymer with randomly placed long branching, even while it also has some short branching; the ratio of long to short branching depends on the details of the polymerization process. A Linear Low Density Polyethylene (LLDPE, ethylene–butene copolymer) is used as an example for linear polyethylene with short branches not randomly distributed along the main chains, associated with non-homogeneous intermolecular chemical composition distributions. For these LLDPE, the short branches concentration for all molecules is not uniform, and this is sometimes referred to as intermolecular branching distribution [14,15].

2. Experimental

2.1. Materials and samples preparation

A linear polybutadiene was synthesized by anionic polymerization of butadiene under high purity conditions following standard methods [13]. The resulting polybutadiene was subsequently hydrogenated (HPB) in solution of toluene using a Pd supported catalyst. The experimental details were previously reported [16]. The HPB have a molecular structure chemically similar to random ethylene-(butene-1) copolymers with a composition of about 20 CH₃/1000 C. This can be calculated from the amount of 1,2-addition of butadiene (~7%mol/mol) measured in the original PB [13].

Two commercial polyethylenes were used. LDPE (203M) and LLDPE (1045.11B) were supplied by Dow-PBB Polisar (Bahía Blanca, Argentina). About 100 g of each polymer were dissolved in boiling xylene, and quickly precipitated in cool methanol to obtain a fine powder. Most of the antioxidant and other additives are expected to remain in the thus formed xylene–methanol solution. The precipitated polymers were exhaustively dried at room temperature.

2.2. Oxidative degradation procedure

HPB, LDPE and LLDPE samples were molded in the form of 0.4 mm thick sheets, by compression molding at 170 °C. Specimens of about 2 g were put in Petri dishes and aged in air at constant temperature in specially designed ovens at 90 °C, for up to 20 days. Small samples were taken from each specimen once a week or

Table 1

Average molecular weights (g/mol) of the original and modified HPB's with peroxide and irradiated, estimated from MALLS-SEC, fraction gel (%), crystallinity degree (%), crystallization and melting temperature ($^{\circ}\text{C}$) obtained during the modification.

Concentration of peroxide (%)	Mw $\times 10^{-3}$ (g/mol)	Gel (%)	T_c ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	Crystallinity degree (%)
0	81.5	–	93.1	108	39.6
0.05	89.2	–	91.7	107.4	39.0
0.1	94.0	–	92.1	107.4	38.3
0.2	140.0	–	89.6	106.7	37.8
1	189.3	76.0	85.6	105.1	33.4
2	91.2	88.0	78.9	99.2	32.0
<i>Irradiation dose (kGy)</i>					
0	72.0	–	94.4	108.4	29.5
29	53.3	–	94.3	110.1	28.5
56	138.3	–	94.8	109.8	28.4
84	151.7	0.4	94.3	108.9	28.3
138	159.5	39.0	94.6	111.4	28.1

more frequently when needed, for SSA analysis. Samples for SSA analysis were always cut through the whole specimen thickness, and therefore results reflect an average of the molecular changes occurred.

2.3. Peroxide modification procedure

2,5-dimethyl-2,5-di(tert-butyl peroxy)-hexane (DBPH) (Akzo Chemical of Argentina) was used as initiator of the modification process. HPBs in the form of fine powder were impregnated with different amounts of a peroxide-hexane solution. Afterwards, the solvent was evaporated inside a hood. This method provides a homogeneous dispersion of the peroxide on the polymer [2,17], with concentrations ranging from 0.05 to 2% w/w based on the polymer.

Impregnated HPBs were then placed between 3 mm thick steel plates lined with aluminum foils, held apart by a 1 mm thick aluminum frame. Finally, the samples were compression molded between the hot plates of a hydraulic press for 30 min at 170°C . The reaction time necessary to complete the reaction was estimated by performing rheological tests following the method utilized by Bremner et al. [18] for monitoring curing reactions.

2.4. Irradiation procedure

Films of the HPB and LDPE were prepared by compression molding at 150°C using a hydraulic press with thermostatically controlled platens. The samples were molded between 1 mm thick steel plates held apart by 0.5 mm thick brass spacers. The films were inserted into Pyrex tubes in air atmosphere. The total film in each tube was set in order to get equivalent total mass. Subsequently these samples were exposed at room temperature to γ -rays generated by a ^{60}Co source. The sample were irradiated to dose in the range from 29 to 138 kGy, using a dose rate of 8 kGy/h determined by dosimetry with a radiochromic thin-film dosimeter. The error in dose can be estimated in 5%.

2.5. Characterization

2.5.1. Gel content

Gel fraction was determined for irradiated and peroxide treated HPB by soluble extraction with xylene at 125°C . The extraction was performed placing about 30 mg of each sample into a basket made from stainless steel mesh. Then, the baskets were immersed in hot xylene for periods of 6 h. An antioxidant, Irganox 1010, was added to the xylene solution for minimizing the effect of plausible peroxide decomposition. After each of these periods the samples

were dried in a vacuum oven at 60°C until constant weight. The extraction was considered complete when, after two consecutive periods of extraction, there was no detectable change of weight in the dried gel. The total time of extraction varied between 36 h and 48 h depending on the sample. The solvent was changed to fresh solvent between two consecutive extractions.

2.5.2. Size exclusion chromatography (SEC)

This technique was used to determine the molecular weights and molecular weight distribution of the original HPB and the polymers obtained after its modification by irradiation and peroxide attack either below or soluble above the gel point respectively. Table 1 lists the average molecular weights. The SEC runs were made at 135°C using 1,2,4 trichlorobenzene as solvent on a Waters 150-C ALP/GPC having a set of five PLGel columns from Polymer Labs with nominal porous sizes of 10^6 , 10^5 , 10^4 , 10^3 and 500 Å. The chromatograph was equipped with a refractive index (RI) detector and with on-line Multi Angle Light Scattering detector (LS) from Wyatt Technology (Dawn DSP). The average molecular weights, Mn and Mw, were estimated using the program ASTRA provided by Wyatt Technology Corp.

2.5.3. Evaluation of basic thermal behavior

Whole (not extracted) samples were used throughout for all DSC characterization and SSA. Small disc samples (approximately 10 mg) were cut from films of all original and modified materials. The samples were encapsulated in DSC aluminum pans and ultra high purity dry nitrogen was used as an inert atmosphere for conditioning and tests in a Perkin Elmer Pyris 1 calorimeter. A first characterization of the thermal behavior of the polymers was performed on the DSC by cooling and heating runs between 25 and 200°C at a heating rate of $10^{\circ}\text{C}/\text{min}$. In order to erase all previous thermal history all the 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. [19]. Samples were heated and held at 150°C for 5 min. Afterwards, they were cooled down to 40°C at $10^{\circ}\text{C}/\text{min}$ to give an initial standard thermal history. Another heating scan followed, at the same rate, to a selected self-seeding temperature denoted T_s , then kept for 5 min at that temperature before cooling it again down to 40°C at the same rate. The first applied T_s is chosen so that the polymer will only self-nucleate (i.e. T_s would 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 (125°C)). 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 40°C was reached. Melting patterns of the samples thus prepared were recorded at a heating rate of $10^{\circ}\text{C}/\text{min}$. The final heating scan after this thermal fractionation reveals a series of multiple melting peaks (as shown in Fig. 1-a) that are a reflection of the multiple mean lamellar thicknesses obtained.

3. Results and discussion

Some molecular characterization for one of the used polymers is included for the sole purpose of showing that the molecular

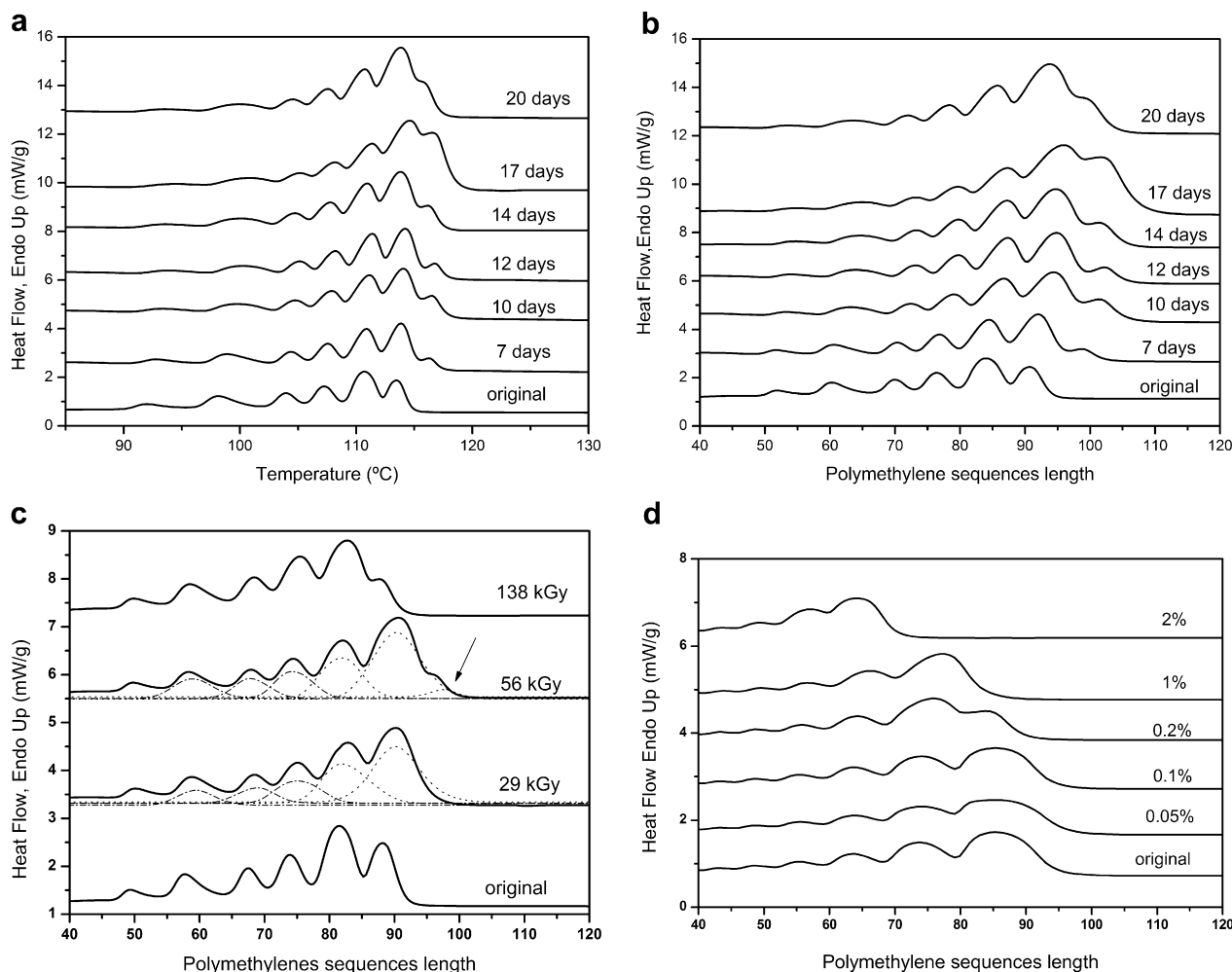


Fig. 1. SSA final endotherms for HPB aged in air at 90 °C a) abscissa is temperature, b) abscissa is polymethylene sequences length, c) irradiated in air at room temperature d) modified with organic peroxide at 170 °C.

structure evolution proceeds following general patterns already established in the literature [3,17,20]. The molecular structures modifications of HPB that undergo attack by free radicals, originated by peroxides decomposition and also by γ -irradiation, is verified to progress according to the crosslinking and scission reactions scheme established for the free radical mechanism [2]. The evolution of weight average molecular weights, gel fraction and some thermal properties for HPB modified with peroxide and irradiated are reported in Table 1. The chain-linking reactions govern the modification process with peroxide; the average molecular weights augment while the crystallinity slightly decreases with the peroxide concentration. Gel formation was detected at the two higher peroxide concentrations. The average molecular weight of the irradiated HPB in air atmosphere decreases with dose over the low dose range; irradiation with higher dose leads to an increase in molecular weight. The formation of a small amount of gel is observed at 84 kGy which grows in proportion with the dose [21,22].

Fig. 1 shows the effect of different attack rates on the HPB, which is used as a model linear low-density polyethylene with homogeneous branching distribution. The HPB is selected for the purpose of avoiding spurious molecular structure inhomogeneities effects – expected to be present in the LLDPE – on the observed SSA spectra. Fig. 1-a) and b) show the original SSA spectra, where the abscissa is temperature, together with the modified SSA spectra where the abscissa has been transformed into polymethylene sequences

length by fitting the experimental data on melting points for linear polymethylenes published by Mandelkern [23]. This type of transformed graph will be used throughout this work, to show the information given by SSA and the molecular structure changes in a more comfortable fashion. The abscissa temperature scale shows some compression of the longer crystallizable polymethylene sequences side, due to the lower slope of the temperature-sequences length graph.

Fig. 1-b) shows the results of attacking the solid HPB structure with oxygen from air at sufficiently high temperatures. Two factors are added here to give an enhanced effect of chain scission, as already mentioned above: low free radicals concentration given by the oxygen, plus higher tertiary carbons concentration in the amorphous phase of the HPB, where most of the oxygen can be found. After only 7 days, extra melting endotherms are added for longer crystallizable polymethylene sequences lengths, given by chains scission at tertiary carbon atoms. The presence of two melting endotherms is merely due to the use of two Ts in this temperature range. Both added endotherms areas increase up to 17 days, and then start to reduce; the reduction may be caused by crosslinking or by secondary carbons scission, as both are more likely to affect first the longest polymethylene sequences. Fig. 1-c) shows results of irradiating solid HPB in air. Mixed effects (crosslinking and scission of main chains) show up quickly, due to a combination of high branching concentration in the amorphous

phase – where the formed free radicals react faster – and overall higher free radicals concentration that reduce the attack selectivity due to the higher radical reaction rate. Thus, an additional melting endotherm for longer polymethylene sequences appears at 56 Kgy, as pointed by an arrow – due to chain scission – and it is soon masked by the chains crosslinking at higher irradiation doses. Fig. 1-d) shows results for HPB melt attacked with free radicals formed by peroxide decomposition at 170 °C. We must here remember that the degradation was performed under a limited amount of oxygen, the one dissolved in the polymer mass before the peroxide attack. The main observed effect for high free radicals concentrations and homogeneous branching points distribution in a homogeneous liquid phase is chains crosslinking, and therefore the original longer polymethylene sequences endotherms quickly disappear.

Fig. 2 also shows the effects of free radicals attack rate, now for the chosen LDPE. For these experiments the used Ts are also evenly spaced, but slightly different to those used for HPB, and so the qualitative conclusions drawn here are equally valid. Fig. 2-a) corresponds to solid LDPE aged in air at 90 °C. Again the chains scission is enhanced by the higher branching points and free radicals concentrations in the amorphous phase, and an extra melting peak shows up for longer polymethylene sequences than the original SSA spectra. Fig. 2-b) shows the combined effects for

higher free radicals concentration, plus the long time elapsed from the irradiation procedure to the SSA experiment, which may allow for free radicals to react inside the crystals. Besides, any free radicals remaining inside the LDPE crystals will react quickly at the

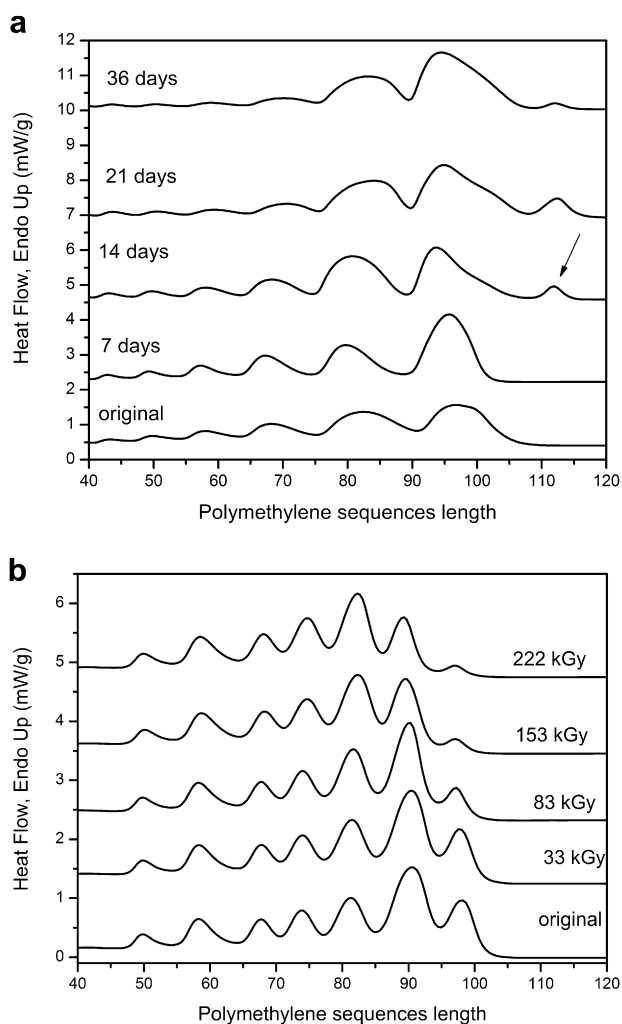


Fig. 2. SSA final endotherms for LDPE a) aged in air at 90 °C and b) modified by irradiation.

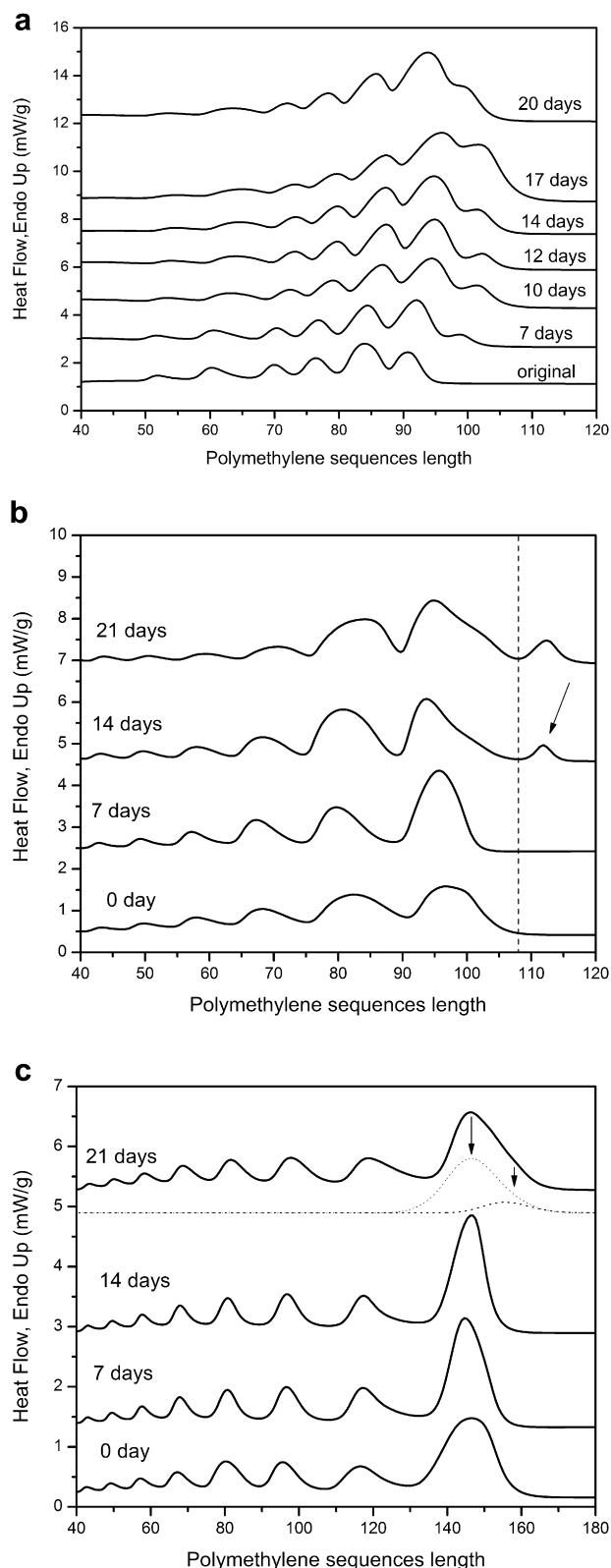


Fig. 3. SSA final endotherms for a) HPB, b) LDPE and c) LLDPE aged in air.

heating stage of the SSA procedure, increasing the chains cross-linking. No extra melting peak shows up for longer polymethylene sequences than the original SSA spectra. The main effect observed is chains crosslinking, evidenced by the continuous reduction of melting areas under the longer polymethylene sequences SSA peaks.

Fig. 3 compares results obtained for HPB, LDPE and LLDPE aged in air at 90 °C. The comparison was chosen to explore effects of branching length and molecular structure distribution or homogeneity. It was first expected that LDPE longer branches might produce larger increases in lamellae thickness when scission events were produced at the tertiary carbon atoms at the branching point. As can be found in the literature [24], LDPE is polymerized as a tree-like random molecular structure with long and short chain branches. HPB shows only short (2 carbon atoms) branches, as does LLDPE. For this type of attack, all three polymers show evidence for chain scission, in the form of added melting endotherms for longer polymethylene sequences than the original polymer. The extra melting endotherm cannot be easily observed for the LLDPE. A deconvolution procedure was used to show the observable peak widening in the form of two peaks. The hardly observable chain scission effect for the LLDPE is due to its non-homogeneous molecular structure distribution, which a) gives a smaller numbers fraction for the longest crystallizable sequences, and b) causes the longest polymethylene sequences endotherms to be placed in the zone for which the melting temperature depends weakly on the polymethylene sequences length [23,25]. HPB and LDPE melting endotherms produced by SSA at the highest Ts are placed in a zone for which the melting temperature changes faster with polymethylene sequences length, and therefore the method seems to be more sensitive for this type of molecular structures. Also a larger concentration effect may be present for the LLDPE when compared with random copolymers: as a more significant fraction of the tertiary carbon atoms neighbor shorter polymethylene sequences lengths, the chain scission added lengths for these short crystallizable sequences will be placed at lower temperatures, therefore being masked by the slower, mixed evolution of these lower melting temperature peaks. Being the thicker lamellae formed first on crystallization, we can imagine that the diffusion processes that contribute to forming thinner lamellae will be increasingly restricted as the crystallization temperatures are reduced, and more precise 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 [12,17]. Unexpectedly, when translated into polymethylene chain lengths, the added SSA melting endotherms for all three different polymers are placed at about 12–14 carbon atoms larger than the original polymer, indicating that the expected effect of the longer branches belonging to the LDPE cannot be easily observed in this type of analysis. The fact that the long LDPE branches are in a very low concentration may be a cause for this. Some authors claim that the long branches to short branches ratio ought to be in the range of 1/10 [26]. This ratio might well account for the complex thermorheological properties of LDPE, and also explain its reduced crystallinity when compared with high density polyethylenes. The effect of longer branches – apparently missing in this study results – will be addressed in a future publication, using model polymers.

4. Conclusions

Using the proposed SSA analysis technique, the selectivity reduction of free radicals attack as its concentration is increased has

been shown. Lower free radicals concentrations favor tertiary carbons scission, and the effect is clearly shown by using the SSA technique. Increasing free radicals concentration produce more random attack on secondary and tertiary carbon atoms, thus increasing the crosslinking rate and reducing the higher temperature melting peaks.

The LDPE and HPB, having random distribution of branches, after free radicals attack show higher melting temperature endotherms in the final SSA thermogram that were not present in those corresponding to the original polymer. These endotherms may be associated to lamellae crystal formed by the crystallization of longer methylene sequences that were hindered to do so in the original polymers.

The hardly observable chain scission effect for the thermally oxidized LLDPE is shown to be due to its non-homogeneous molecular structure distribution as compared with the HPB and LDPE.

The influence of the scission process on the thermal behavior was also observed in the case of the HPB irradiated under air atmosphere. On the contrary, the HPB modified with peroxide as well as the irradiated LDPE showed mainly chain crosslinking identified by a reduction of the area of the higher melting endotherms in the final SSA thermogram.

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