

Mechanism and molecular weight model for thermal oxidation of linear ethylene–butene copolymer

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Abstract

The mechanism of thermooxidative degradation at 80°C of a narrow distribution linear ethylene–butene copolymer has been described by determining the chemical modifications and molecular weight distribution changes occurring in the polymer chains, and successively fitting the experimental results with a mathematical model which allows scission and crosslinking reactions to occur simultaneously. Degradation takes place with autoacceleration and from the computer simulation a cubic dependence of the degree of crosslinking and degree of scission with exposure time was obtained. It was established that in this system scissions predominate over crosslinking, in accordance with the drop in average molecular weights and the concomitant accumulation of oxidation products. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Olefin copolymers; Ethylene–butene copolymer; Thermal oxidation

1. Introduction

Thermal oxidation of polyethylene and related copolymers has been the object of many studies. The process is controlled by fast reactions between atmospheric oxygen and the radicals formed in the polymer molecules, with the production of a series of new functional groups in the macromolecular structure [1–5]. In addition to reactions which incorporate oxygen atoms, and eventually also as a consequence of the reactivity induced by the oxidized structures, chain scission and crosslinking reactions also take place, greatly influencing the sample molecular weight distributions. All these reactions are considered to occur simultaneously, and their relative importance depends on sample structure, morphology and environmental conditions.

Polymer physical properties are extremely sensitive to molecular weight distributions and molecular architectures, and therefore chain scission and crosslinking reactions have an important effect on polymer performance. For this reason, in the study of oxidative degradation of a polymer it is important to evaluate not only the chemical changes which take place but also the way molecular weight distributions

change, in order to understand the influence of such processes on end-use material properties.

The formation and evolution, during polymer degradation, of chains with higher and lower molecular weights (resulting from coupling or crosslinking reactions and from scissions, respectively) is conveniently monitored by size exclusion chromatography (SEC). The best sensitivity conditions are attained with the use of samples that initially have narrow molecular weight distributions. Several studies dealing with degradations where chain scissions are practically the only reactions involved have already been reported, and the reaction mechanisms were investigated by comparing the experimental results of molecular weight distribution changes with those obtained from Monte Carlo simulations [6–9]. In other types of polymer degradation, as in oxidation or high energy radiation, simultaneous scission and crosslinking must be taken into account, and examples of quantitative analysis of the changes occurring in samples of γ -irradiated hydrogenated polybutadienes (HPBs) of narrow initial distribution have been successfully reported with the application of a proper mathematical model [10–12].

In this work we have investigated the thermooxidative degradation of a narrow distribution linear ethylene–butene copolymer at 80°C obtained from the catalytic hydrogenation of practically monodisperse linear polybutadiene. Sample degradation was followed in time by determining

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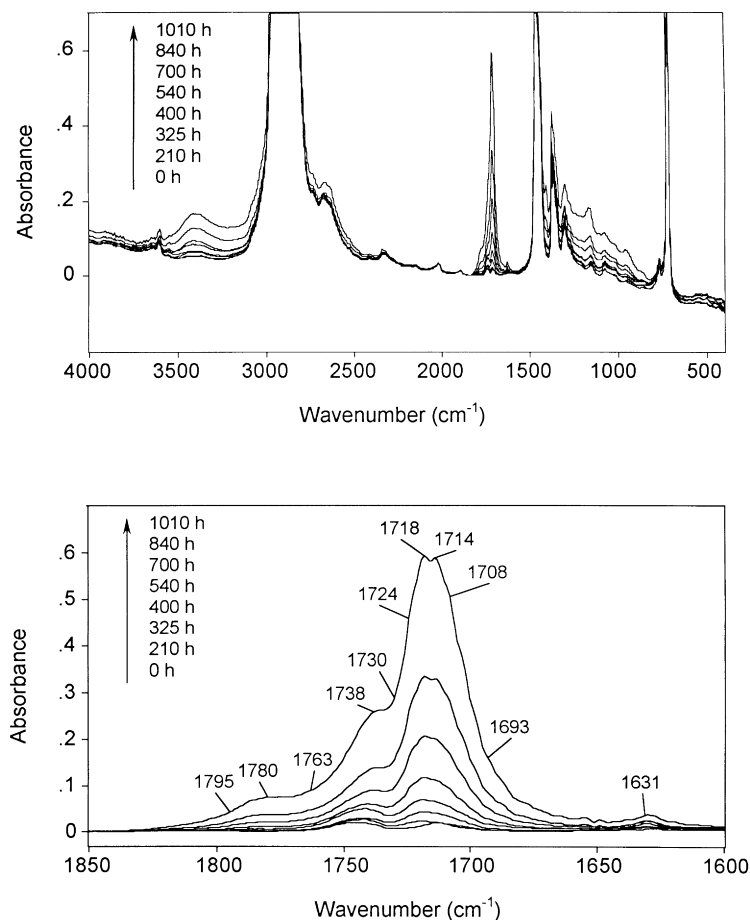


Fig. 1. FTIR spectra of HPB before and after different times of thermal treatment in air at 80°C.

the chemical changes with infrared spectroscopy (FTIR) and the molecular weight distribution variations by SEC. A mathematical model previously derived [12] was adapted to this particular case and used to fit the experimental results in order to obtain the quantitative description of the degradation process. The evolution of sample molecular weight distribution during degradation could be connected with the structural changes derived from the oxidation reactions.

2. Experimental

Linear polybutadiene was synthesized by anionic polymerization under high purity conditions in a vacuum system. The practically monodisperse polymer was catalytically hydrogenated in solution in a high pressure reactor (Parr).

Thin films (100–120 μm) were made by pressing 0.2–0.3 g of the HPB between Teflon sheets at 160°C for 2 min. The films showed no sign of oxidation after preparation. The polymer films were placed in a forced air circulating oven kept at 80°C. At each selected time, one film was taken from the oven and the FTIR and SEC characterization measurements were performed.

FTIR was done on a Perkin–Elmer 1710 instrument with a DTGS detector and 4 cm^{-1} resolution. Spectral acquisitions and data treatments were performed with Spectra Calc (Galactic Industries, USA) software. In order to compare spectra measured on different films, thickness normalization was performed on the spectra by taking the absorption at 2020 cm^{-1} as a reference.

SEC measurements were performed in a Waters 150-C ALC/GPC connected in line with a multi-angle laser light scattering apparatus (MALLS) Wyatt Dawn DSP. The entire ensemble was operated at 135°C with a flow rate of 1 ml/min. Trichlorobenzene (TCB) was used as solvent. A set of three PL gel columns was used, with nominal pore sizes of 10⁶, 10⁴ and 500 Å. One guard column preceded this set. The two-instrument ensemble contained two detectors, a differential refractive index cell (DRI) and the MALLS. Data processing was performed in two ways, either taking advantage of the MALLS detector or ignoring it and using the traditional universal calibration curve with the DRI signal. Polystyrene (PS) standards were used in the construction of the calibration curve. The Mark–Houwink constants K and a needed to convert PS data to PE data were: $K_{\text{PS}} = 1.21 \times 10^{-4}$ dl/g; $a_{\text{PS}} = 0.707$; $K_{\text{PE}} = 4.06 \times 10^{-4}$ dl/g; $a_{\text{PE}} = 0.725$. These values were taken from the literature [13].

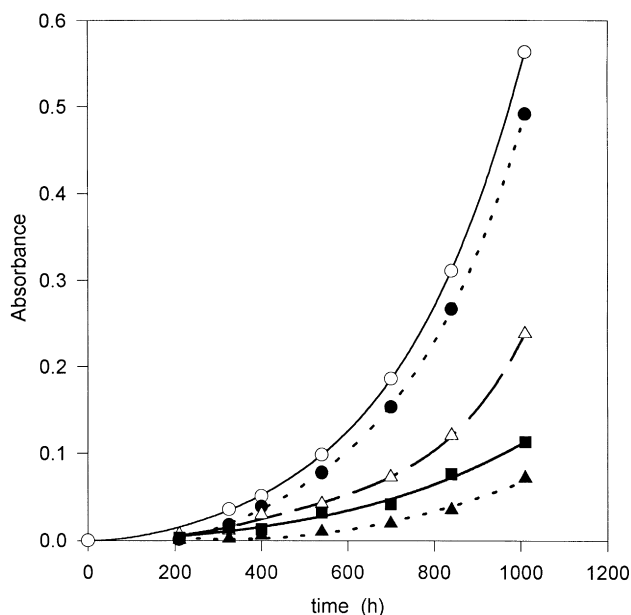


Fig. 2. Normalized absorbance values of the principal functional groups from oxidation of HPB at 80°C. ○: ketones; ●: carboxylic acids; △: esters; ■: hydroxyls; ▲: lactones.

The physical constants needed for the MALLS calculations were the Rayleigh ratio of TCB, $R_{\theta} = 3.57 \times 10^{-5}$ [14], the refractive index of pure TCB at 135°C, $n_0 = 1.502$ and the refractive index increment of PE in TCB at 135°C, $dn/dc = 0.104 \text{ cm}^3/\text{[15]}$.

3. Results and discussion

The FTIR spectra in Fig. 1 show the structural changes that occur during the thermal treatment of the HPB at 80°C in air for 1010 h. Important spectral modifications develop in the sample, due to the new functional groups formed during the oxidative degradation. In the high frequency region the small peak at 3555 cm^{-1} is attributed to relatively stable hydroperoxides, and the broad absorption centered around 3400 cm^{-1} to extensively associated hydroxyl

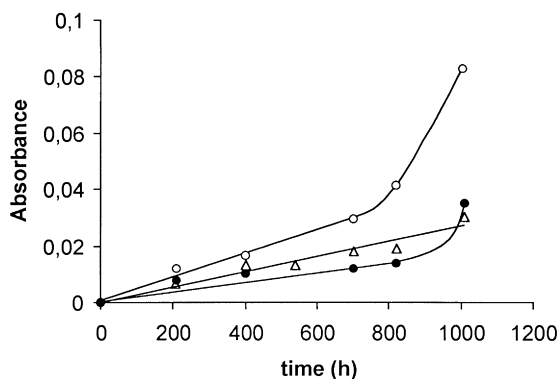


Fig. 3. Formation of double bonds. △: 1630 cm^{-1} ; ○: 960 cm^{-1} . ●: 875 cm^{-1} .

groups [2,4]. In the carbonyl region a strong complex absorption is formed, where the following components can be assigned [2,4,5,16]: open chain anhydride groups at 1795 cm^{-1} ; γ -lactones and peracids at ca. 1780 cm^{-1} ; ester groups at $1745\text{--}1740 \text{ cm}^{-1}$; aldehyde groups contribute to the absorption around 1730 cm^{-1} . The peak maximum at 1718 cm^{-1} is attributed to ketone groups, and the absorptions in the range $1710\text{--}1700 \text{ cm}^{-1}$ to carboxylic acids. Unsaturated ketones contribute to the absorption in the range $1695\text{--}1685 \text{ cm}^{-1}$ [2].

The small peak at 1630 cm^{-1} is due to the stretching mode of carbon–carbon unsaturations. Different types of C=C double bonds are formed in the degradation of polymer chains — the peak visible at 960 cm^{-1} is characteristic of the vinylenes groups, whereas that at 875 cm^{-1} comes from vinylidene unsaturations [4,17]. Absorption of vinyl groups is at 910 cm^{-1} and appears in our spectra only as a shoulder.

In Figs. 2 and 3 it is shown how the normalized infrared absorbances of the principal functional groups evolve with time of treatment. All the carbonyl structures present a similar trend, consistent with an autocatalytic increasing rate of formation. The same autocatalytic behavior was reported for the thermal oxidation of a commercial LLDPE [4]. Double bonds, on the other hand (Fig. 3) start to develop from the beginning of the treatments, with a constant formation rate in the interval up to ca. 800 h.

The sample molecular weight distribution changes were measured in parallel to the evolution of chemical structures by SEC with DRI and MALLS detectors. The data were evaluated both by treating the DRI trace with a universal calibration curve, and with the absolute light scattering data. The HPB samples were completely soluble after all treatment times, and the molecular weight characterization results are reported in Table 1. Each value is the average of at least two measurements. No large difference exists between the reported molecular weights obtained through the two methods just described. This type of behavior has already been described for polymers with low polydispersity [18].

Table 1
Average molecular weights at different times of treatment, as measured through the use of two different detectors

Time (h)	DRI and universal calibration			DRI and LALLS		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
0	78,900	85,700	1.09	69,300	74,200	1.07
120	63,800	73,200	1.15	59,900	69,600	1.16
210	62,600	72,400	1.16	61,500	69,600	1.13
325	47,000	66,700	1.26	51,500	62,400	1.21
400	30,500	64,700	1.37	49,300	64,700	1.31
540	29,300	60,000	1.97	30,200	58,900	1.95
700	16,000	42,400	2.66	16,900	37,700	2.23
840	14,200	35,500	2.51	15,800	32,700	2.07
1010	8200	22,300	2.73	9200	20,500	2.23

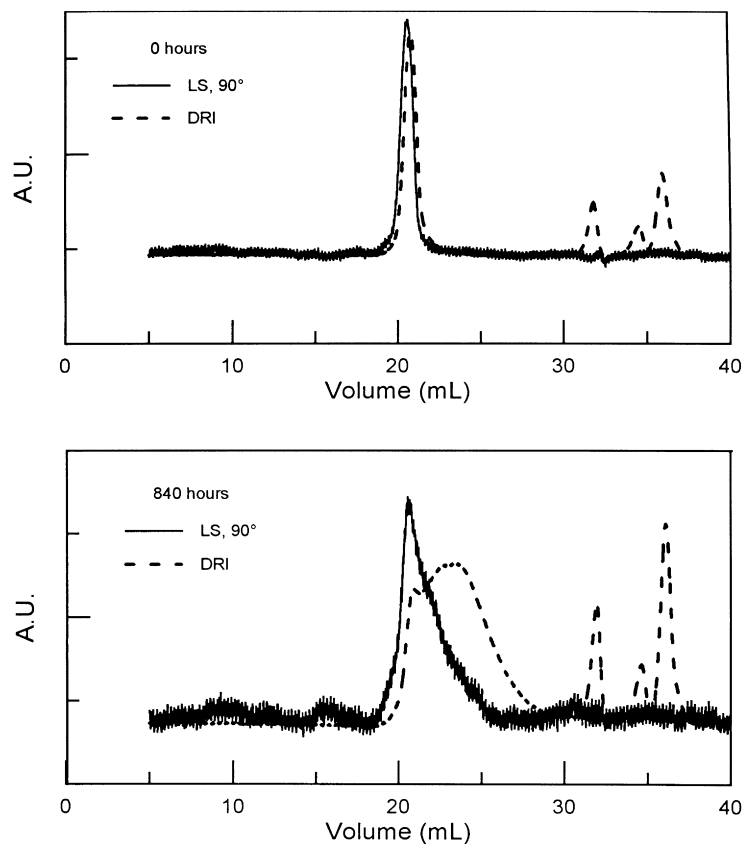


Fig. 4. SEC chromatograms of initial HPB (top) and after 840 h thermooxidation (bottom).

We show in Fig. 4 the SEC traces of the HPB sample before treatment and after 840 h of thermal oxidation. The narrow initial molecular weight distribution of the polymer and the distribution broadening towards the region of lower molecular weights may be clearly seen, indicating that scission reactions are certainly predominant during the degradation.

The scission reactions have a direct influence on M_n , and the number of apparent chain scissions per molecule, S , can be obtained from the relationship

$$S = (M_{n,0}/M_{n,t}) - 1 \quad (1)$$

where $M_{n,0}$ and $M_{n,t}$ are the number average molecular weights at times zero and t , respectively.

In degradation processes occurring with random scissions the relationship between S and t is linear [19]. In the case of HPB the apparent number of chain scissions, calculated from the M_n values of Fig. 5 grow with time in the way illustrated in Fig. 5, showing a slow initial increase, up to ca. 200 h, followed by an autocatalytic growth. This trend closely resembles that of the formation of carbonyl structures, previously shown.

4. Mechanism and model

In the thermooxidative degradation of HPB at 80°C the

different types of carbon–carbon unsaturations develop from the beginning, without any induction period and before the appearance of oxidized structures.

By taking into account the molar absorptivities reported

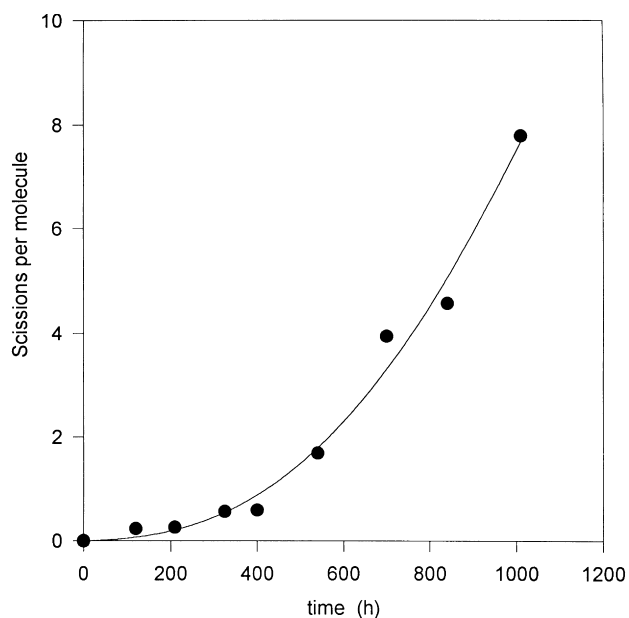
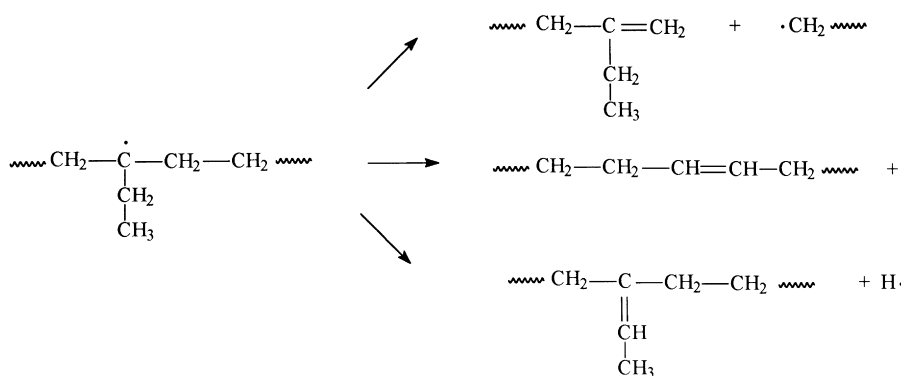


Fig. 5. Apparent number of chain scissions in the thermal oxidation of HPB.



Scheme 1.

for vinylenes, vinylidenes [4], and that of the C=C stretching vibration around 1630 cm^{-1} [20], the relative amounts of the different structures were established from the initial slopes of the lines in Fig. 3. The absorption at 1630 cm^{-1} was considered representative of the total C=C population, and by subtracting from it the contribution of the two other groups the content of vinyl groups was calculated. Unsaturation was evaluated to be present in the approximate ratio *vinylene:vinyl:vinylidene* = 3:2:1.

The principal reactions responsible for these structures take place on tertiary or secondary radicals formed in the polymer chains in the initiation step. In the first case, reported in Scheme 1, vinylidenes, vinylenes and also ethylidenes may be produced. Only the vinylidene formation reaction occurs together with a chain scission. The secondary radicals induce formation of vinylenes and of vinyl groups, the latter resulting from chain scissions (Scheme 2). Vinyl groups and chain scissions can also derive from reactions of allylic radicals produced in positions adjacent to the vinylenes (Scheme 3).

By considering the calculated ratios of different unsaturations it turns out that ca. 50% of them must be accompanied by chain scissions. However, direct correlation between unsaturation content and number of chain scissions determined through the M_n values cannot be established because at this reaction stage, radical recombination reactions with crosslinking also take place.

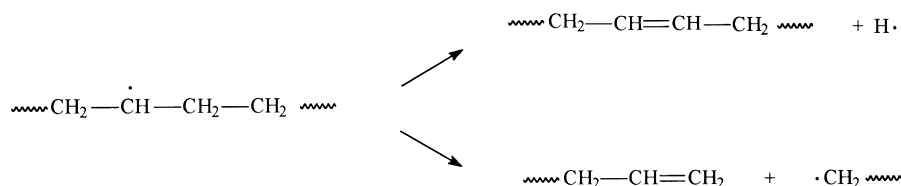
As far as the structures formed in the oxidation reactions are concerned, a ranking between different groups may be obtained by looking at the kinetic curves of Fig. 2. By considering that acid, ester and lactone groups show in the infrared region similar absorption coefficients, whereas

absorptivity of ketone groups is about 40% lower [4,5], the yield of carbonyl containing compounds is in the order: ketones > acids > esters > lactones, in full agreement with the literature results for thermal oxidation under similar conditions [4].

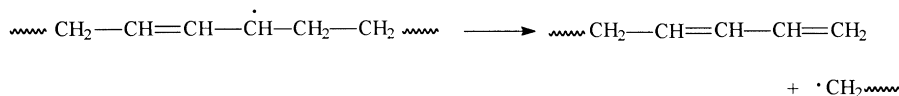
In HPB the formation of a ketone group may take place, according to Scheme 4, at the same time with a chain scission when oxidation occurs at the tertiary carbon atom. Other types of chain scissions may develop from oxidation of the methylene groups in the polymer chains, as shown in Scheme 5, leading to the formation of aldehydes and carboxylic acids. The lactones also are a consequence of chain scissions, as they are produced from intramolecular reactions of γ -hydroxy acids [21].

From all the above results, one may envision a degradation mechanism where the rate of chain scissions must increase with the accumulation of carbonyl groups. The coupling and crosslinking reactions which are also supposed to take place, on the other hand, may be assessed and quantified by simulating the degradation process from the point of view of the molecular weight distribution changes with a computer model.

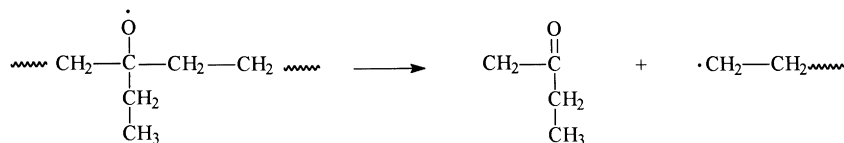
We have modeled this system using an extension of a mathematical model previously presented [12]. In this model, both crosslinking and scission are allowed to occur simultaneously. For modeling purposes, crosslinking is expressed as a fractional conversion α , that measures the number fraction of all reactive sites that have undergone crosslinking. Similarly, a fractional conversion β is used to characterize the scission reaction. Both reactions are assumed to be independent. Details may be found elsewhere [12]. For this work, the measured data on M_n were used to



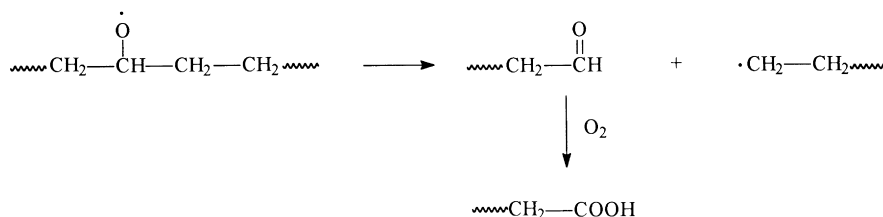
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

express β as a function of treatment time. A polynomial of order three gave the best fit through a least squares procedure. The fractional conversion α was expressed as a fraction of β , using the relationship

$$\alpha = m\beta \quad (2)$$

where m is a constant. In this way $\alpha + \beta$ was expressed as a polynomial function of exposure time. This made it different from the previously reported model, where $\alpha + \beta$ was

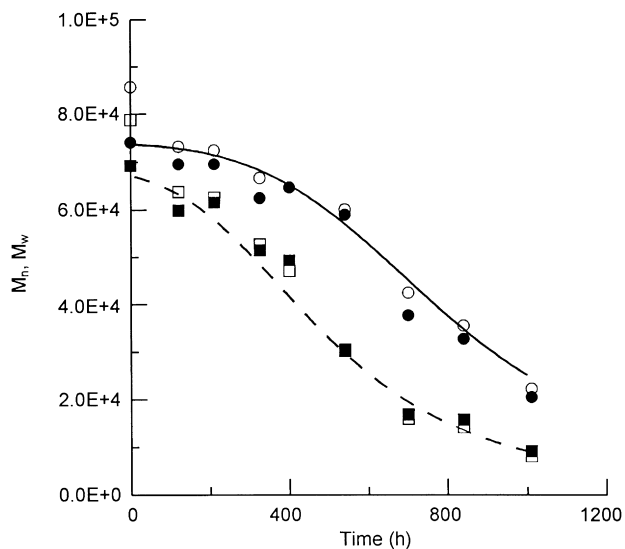


Fig. 6. Measured number average (squares) and weight average (circles) molecular weight of the treated samples compared with the theoretical calculations (lines). Hollow symbols correspond to the DRI detector, while full symbols correspond to the LS detector.

assumed to be directly proportional to the time of exposure as it is usual for γ irradiated systems.

The development of carbonyl groups (Fig. 2) and especially the trend of apparent number of chain scissions (Fig. 3) does indeed give indications that the reactions tend to accelerate with time.

The process was modeled assuming the cubic function mentioned above, and good agreement between theory and experiment was obtained. The results are shown in Fig. 6. These curves were found assuming a negative binomial distribution for the untreated polymer, with initial M_n and M_w values corresponding to those measured using the light scattering detector, and an m value of 0.2 in Eq. (2) mentioned earlier. It is not surprising to find that M_n values adjust well to the theory, since they were used to find the dependence of β with time. The agreement of M_w values is what confirms that our model is a good representation of what happens with the samples.

5. Conclusions

The thermal oxidation of a linear ethylene–butene model copolymer has been investigated by determining the chemical modifications induced in the polymer chains and by correlating the sample molecular weight distribution changes with a non-constant in the time scission-crosslinking process. The autoacceleration character of the oxidation reactions has been modeled with a cubic dependence of the degree of crosslinking and the degree of scission with exposure time. In this system scission predominates over crosslinking, as indicated both by the drop in average molecular

weights and the concomitant accumulation of oxidation products whose formation is favored by chain scissions. One relevant result of this work is that the detection and quantification of crosslinking reactions has been only possible through the molecular weight modeling and computer simulation of the degradation process.

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