Crystallization behavior of random ethylene–butene copolymers modified with organic peroxide

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ABSTRACT

The effect of molecular cross-linking on the crystallization of random ethylene–1-butene copolymers obtained from hydrogenation of model polybutadiene was studied by means of differential scanning calorimetry. The copolymers were modified with different concentrations of organic peroxide in the molten state to generate different crosslink levels. Under isothermal conditions, the crystallization rate of the modified polymers decreased with the average molecular weight likewise to that observed in the unmodified copolymers. Original and modified polymers show similar isothermal crystallization rates when compared to equivalent weight average molecular weights. Under no isothermal crystallization conditions, the temperature and the enthalpy of crystallization of the modified polymer decreased almost linearly with the concentration of peroxide. The activation energy for crystallization increased with the concentration of peroxide indicating that the increment in molecular crosslinking restricts the crystallization process.

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1. Introduction

The modification of ethylene based polymers using organic peroxides is a method extensively used to improve their thermo-mechanical stability, wear and chemical resistance [1–3]. The method is based on generating macro-radicals that follow mainly combination reactions given rise to linkages between the chains of the polymer. It is known that when the polymer undergoes chain-linking, the molar mass increases with the concentration of the peroxide to reach infinitely large values. If the peroxide concentration increases further, a molecular network or gel forms, and this phenomenon is called gelation. Beyond the gelation, the gel grows with increasing the concentration of peroxide becoming a large fraction of the total mass. The changes in molecular structure affect the semicrystalline morphology that, together with the adopted crystallization process, determines the physical and mechanical properties of the material [1–3].

The influence of the molecular structure on the crystallization behavior of polyethylene and ethylene copolymers has been extensively studied in the past [4–20]. It is known that the average molecular weight, average molecular weight distribution, co-monomer content and composition distribution are important

variables in controlling the crystallization behavior of the polymers. For instance, at a given crystallization temperature, the crystallization rate of linear polyethylene and ethylene copolymers passes through a minimum when is plotted as a function of the weight average molecular weight [5,6]. In addition, the increment in comonomer concentration and the presence of long-chain branches in the molecular structure reduce the overall crystallization rate compared to that of a linear polymer with equivalent molar mass [4,7–15]. In the case of polymers with star like molecular architectures, it has been observed that it can crystallize slower or faster than a linear polymer with comparable molecular weight depending on the molecular weight of the branches [5,12]. The effect of crosslinking on the thermal properties and crystallization behavior of polyethylene has also received some attention in the past although the reports are still limited [16,21–27]. Most of the studies analyzed the influence of the molecular network on the crystallization process. In general, it was observed that the increase in the amount of gel reduces the crystallization rate, the crystallization temperature and the degree of crystallinity.

The aim of this work is to study the crystallization behavior of random ethylene–butene copolymers obtained from the hydrogenation of model polybutadiene (HPB), whose molecular structures are modified by chemical reactions initiated with organic peroxide. This article follows our previous works dealing on the influence of the modification on rheological properties and self annealing crystallization behavior of the modified copolymers [28–30]. The previous works have demonstrated that when concentrations

Table 1
Average molecular weights (g/mol) from MALLS-SEC, gel amount (wt%) and mass percentage of low and high molecular weight fractions.

Polymer	Peroxide concentration (wt%)	Mn ($\times 10^{-3}$) (g/mol)	Mw ($\times 10^{-3}$) (g/mol)	Gel (wt%)	Low molecular weight fraction (wt%)	High molecular weight fraction (wt%)
P81	0	80 ± 3	81 ± 3			
P81-0.05	0.05	76 ± 4	89 ± 7		5	10
P81-0.1	0.1	81 ± 5	94 ± 8		8	25
P81-0.5	0.5			43 ± 3		
P81-1.0	1.0			85 ± 5		
P103	0	99 ± 2	100 ± 3			
P103-0.05	0.05	100 ± 4	110 ± 5		5	10
P103-0.1	0.1	119 ± 5	154 ± 8		7	30
P114	0	108 ± 2	114 ± 2			
P114-0.05	0.05	114 ± 3	118 ± 4		5	15
P114-0.1	0.1	122 ± 3	167 ± 2		8	35

of peroxide below the gel point were employed, the weight-average molecular weight of the modified copolymers augments, the molecular weight distribution gets wider and long chain branched structures are formed as the concentration of peroxide increases. Beyond the onset of gelation, the gel amount increases continuously with the peroxide concentration. The molecular characteristics of the modified HPB allow studying these systems to increase the data available on the crystallization behavior of polyethylene from the melt. The crystallization process was studied by differential scanning calorimetry (DSC) under isothermal and non isothermal conditions. The isothermal treatment was applied just to modified samples with concentration of peroxide below the critical dose.

2. Experimental

2.1. Materials

The HPB's were obtained by hydrogenation of polybutadienes that were synthesized by anionic polymerization of butadiene. The synthesis and hydrogenation method were already reported [29]. The copolymers have a composition of about 20CH₃/1000C that was inferred from FTIR spectra of the polybutadiene precursor that revealed that about 7% of the butadiene molecules were added to the growing chain of all the polybutadienes following a 1,2-addition path.

The average molecular weight of original and modified polymers was obtained by analyzing size exclusion chromatograms (SEC) obtained using 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 A, and equipped with on-line MALLS (multi angle light scattering detector) from Wyatt Technology (Dawn DSP). The test was carried out at 135 °C, using 1,2,4 trichlorobenzene as solvent. The molecular weights were estimated using the ASTRA program developed by Wyatt Technology Corp. Table 1 lists the polymers used in this study and their average molecular weight. The polymers are named P#, where # identifies the weight average molecular weight of the original polymer. By other hand, the modified polymers are named as P#-X, where X identifies the peroxide concentration used, thus P81-1 means that the polymer P81 was modified with 1.00 wt% of peroxide.

2.2. Modification procedure

The 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane peroxide, used as initiator of the modification process, was kindly supplied by Akzo Chemical of Argentina. The HPB's, in the form of fine powder, were impregnated with different amounts of peroxide–hexane solution. The hexane was allowed to evaporate over a period of 16 h under hood to obtain the desired final concentrations of peroxide in the polymer. Various authors have used this method because it

provides a homogeneous dispersion of the peroxide on the polymer [27,28].

The polymer thus impregnated was placed between 3 mm thick steel plates lined with aluminum foils and held apart by a 1 mm thick brass frame. The sample was then compression molded between the hot plates of a hydraulic press at 170 °C for 32 min. The reaction time was eight times larger than the halftime of the peroxide at the temperature of reaction, which is 4 min according to the technical information given by the supplier.

The polymers P81 and P114 were modified with peroxide concentration above the gel point. For these samples the gel fraction was determined by extracting the soluble portion of different specimens of each modified polymer with xylene at 125 °C. The extraction was performed by placing a given amount of each sample (between 0.4 and 0.8 g) into a basket made either from stainless steel mesh or cellulose. The baskets were immersed in hot xylene for different periods of 4 h. After each period, the specimens were dried to constant weight in vacuum oven. 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 and 72 h depending on the sample. Fresh solvent was used in every extraction period. In order to prevent oxidation of the samples, nitrogen gas was bubbled continuously into the system and a small amount of Irganox 1010 was added as antioxidant. The solution, which contains the soluble part, was poured into cool methanol to precipitate the extracted material. The produced gel amount was included in Table 1.

2.3. Differential scanning calorimetric tests

Isothermal and non-isothermal crystallization tests were carried out in a Perkin Elmer Pyris 2 DSC. Pure indium was used as a reference material to calibrate both the temperature scale and the melting enthalpy. All DSC runs were performed under nitrogen atmosphere. Samples of approximately 6.0 ± 0.1 mg were placed in aluminum pans and loaded at 25 °C to the DSC, heated up rapidly to 160 °C and maintained at this temperature for 5 min to remove thermal history. In the case of isothermal crystallization studies, the melted samples were rapidly (40 °C/min) cooled down to the required crystallization temperature (98–104 °C) and allowed to crystallize during 10 min. The non-isothermal crystallization studies were carried out by cooling the samples down to −35 °C using constant cooling rates of 5, 10, 20 and 30 °C/min. In all cases, the samples were kept at 160 °C for 3 min prior to cooling. For each material minimum of three crystallization experiments were performed.

3. Results and discussion

The average molecular weights of the HPB were 81,000, 103,000 and 114,000 g/mol for P81, P103 and P114, respectively, while
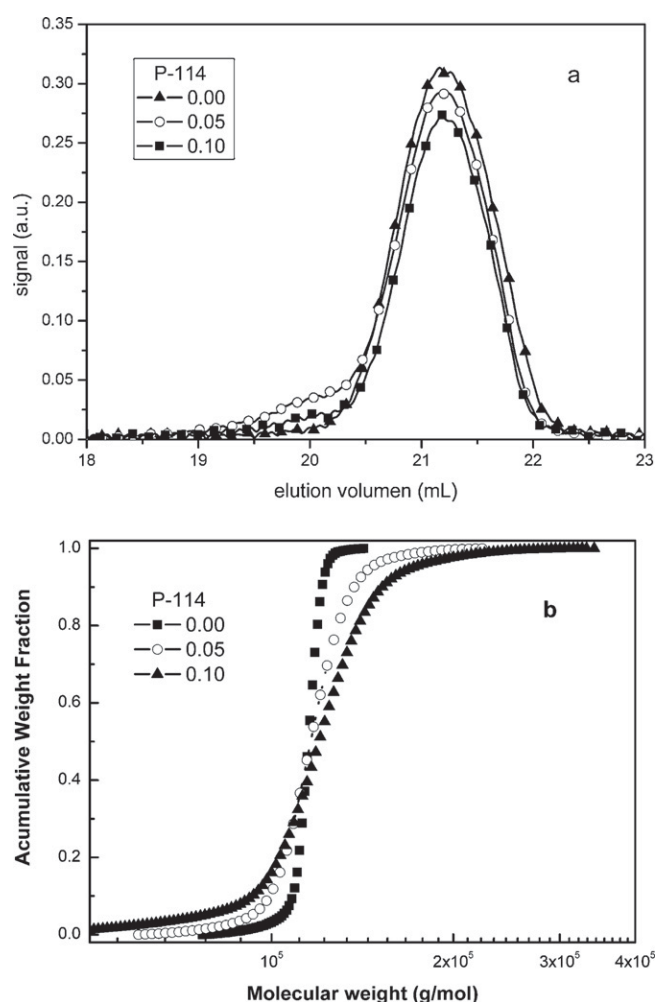
Fig. 1. SEC trace and cumulative weight fraction of original P114 and modified with 0.05 and 0.10 wt% of peroxide.

the polydispersity was lower than 1.1 in all the cases. Significant changes in the molecular weights distribution of the original polymers were observed when the polymers were modified with peroxide concentration below the gel point [28–30]. The modification produced similar changes qualitatively in the molar mass distribution of the studied polymers. As an example, Fig. 1 shows SEC trace and cumulative weight fraction curve of the polymers obtained from the modification of P114; which were chosen as illustrative examples of the changes in the molecular weight distribution that occurs due to the modification. It can be observed, by analyzing the high molecular weight side of the curves of Fig. 1a, the formation of a population of molecules having molar masses about twice or three times larger than the original one. These new species are consequence of combined reactions between macroradicals producing branched macromolecules with a complex architecture. Fig. 1b shows the accumulative weight fraction curves obtained for the polymers whose SEC traces are shown in Fig. 1a. It can be observed, in Fig. 1b, that the mass of the species with molecular weight larger than the original one can be up to 30% of the total mass when the highest peroxide concentration was used. The modification also produces a small fraction of molecules with molecular weights lower than that corresponding to the original polymer, which results from a chain-scission process. For instance, a low molecular weight fraction amount of about 8% of the total mass for the P114-01 can be observed. Table 1 also reports the mass percentage of molecules having molar masses lower than those contained
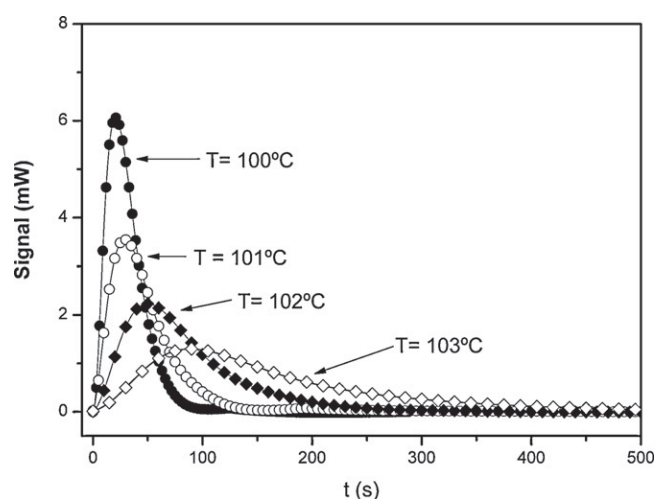

Fig. 2. Crystallization exotherms (DSC) for P-81 obtained at the indicated temperatures.

in the original polymer. Consequently, the molecular structure of the modified polymer is formed by a blend of new species generated by chain linking, scission and molecules that remained unchanged with respect to its initial molar mass [28–30].

The measured average molecular weights of the modified polymer as well as the percentage of gel produced in the samples are included in Table 1. The gel amount increases with the peroxide concentration and, as expected, the lower the molecular weight the higher the peroxide concentration necessary to generate a similar proportion of gel in the material [1,3,24,28].

3.1. Isothermal crystallization

In order to compare the crystallization kinetics of the polymers isothermal crystallization experiments were carried out at several temperatures in the range from 98 °C to 104 °C. This temperature range was chosen as well defined crystallization exotherms can be obtained like the ones displayed in Fig. 2 that corresponds to P-81 polymer. The set of exotherms have the characteristics feature observed in the crystallization of all the polymers. The beginning of the crystallization and the location of the peak maximum shifted towards higher times as the crystallization temperature increased, indicating that the rate of crystallization decreases with temperature, which is a characteristic feature of nucleation controlled growth of crystal [5,6]. Table 2 displays the heat of crystallization obtained from integration of the exotherms at some of the isothermal temperatures used. It can be observed that the heat of crystallization slightly decreased with the temperature for a given polymer, while it decreases with the augment in the molecular weight at a given crystallization temperature. The reported results are in accordance with that commonly observed in the

Table 2
Heat of crystallization for some original and modified HPB's as a function of crystallization temperature.

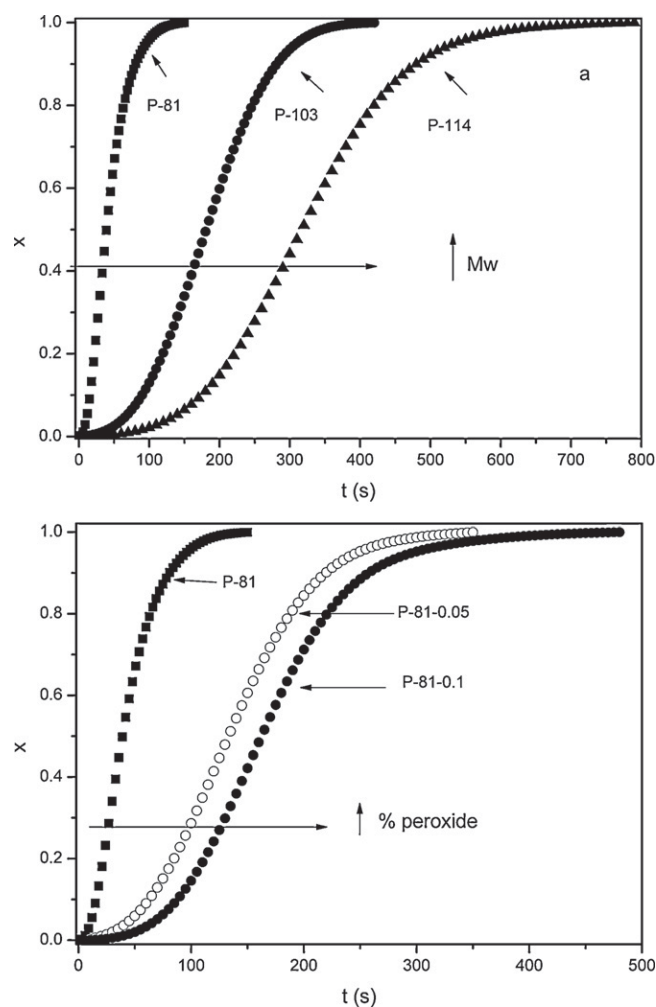| Polymer	ΔH (J/g)			
	100 °C	101 °C	102 °C	103 °C
P81	46	44	38	36
P81-0.05	44	43	42	40
P81-0.1	44	40	38	37
P114	41	38	35	33
P114-0.05	40	38	34	32
P114-0.1	38	37	33	30

Fig. 3. Crystallization isotherms obtained at 101 °C for (a) HPB with different molecular weights and (b) P81 with different peroxide concentrations.

Fig. 4. Plots of $\log(-\ln(1-X))$ as a function of $\log t$ for (a) original P81 and (b) P81 with 0.10 wt% of peroxide.

crystallization of random copolymer that is associated to the limitation in the fraction of ethylene sequences that can form part of the crystalline phase as the isothermal crystallization temperature increases [7]. The degree of crystallinity developed during the crystallization can be estimated comparing the heat of crystallization with that associated to perfect crystal 288 J/g [4]. So, the degree of crystallinity ranges from 10% to 20%, depending of the molecular weight and also on the crystallization temperature.

The relative weight fraction of the crystallized part X was evaluated from the exothermic peak using the following equation:

$$X = \frac{\Delta H_t}{\Delta H_{total}} \tag{1}$$

where ΔH_t and ΔH_{total} are obtained from integration of the crystallization exotherms and represent the portion of exothermic heat at time t, and total exothermic heat measured at the end of the transformation process respectively. Fig. 3 shows the crystallization isotherms obtained at 101 °C for HPB's with different molecular weights (Fig. 3a) and for P-81 and the P-81 modified with different peroxide concentrations (Fig. 3b). The isotherms have an S-shape that is typically observed in nucleation and growth crystallization processes. As expected, the temperature interval over which isothermal crystallization can take place shifted to high temperature as the molecular weight of the polymer is increased [5,6].
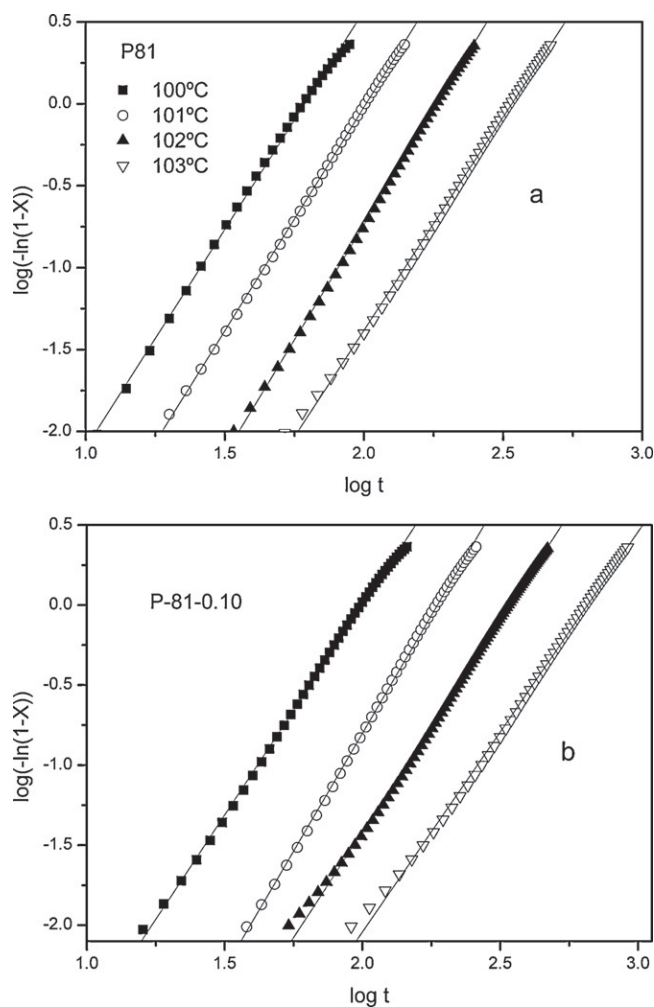
The crystallization curves were analyzed by following the theory of Avrami adapted to the crystallization kinetics of polymers [4]. The general form of the Avrami's equation is given by:

$$X = 1 - \exp(-k \cdot t^n) \tag{2}$$

where n is a coefficient that can be related to the geometry of the growing crystals and the nucleation conditions, and k is an overall crystallization rate constant. In order to analyze the crystallization kinetic data following the Avrami formalism plots of $\log[-\ln(1-X)]$ as a function of $\log(t)$ were set up. As example in Fig. 4 the data results for P81 and P81-0.10 are presented over the relative crystallinity range from about 0.1–0.4. We found that, in this range of relative crystallinity, Avrami equation can describe the crystallization process and a good linear fit of the data can be obtained. The solid lines in the plots represent the best fit of the experimental data. The obtained fitting parameters n and k are presented in Table 3. The table also includes the crystallization half-time ($t_{1/2}$) that was defined as the time needed to reach the 50% of the total crystallinity computed since the sample reaches the isothermal temperature.

The Avrami exponent n is usually used as indicative of the type of nucleation and growth process that prevails in the crystallization process. Table 3 shows that n take values between 3 and 3.6 in the range of temperatures analyzed. The values of n found here are consistent with several combinations of crystallization processes so it does not allow suggesting a polymer crystallization mechanism [4].

Table 3
Results of the Avrami and half time related of original and modified HPB's at different temperatures.

Polymer	Temperature (°C)											
	100			101			102			103		
	n	$k\,(\times 10^6)$	$t_{1/2}$ (s)	n	$k\,(\times 10^6)$	$t_{1/2}$ (s)	n	$k\,(\times 10^6)$	$t_{1/2}$ (s)	n	$k\,(\times 10^6)$	$t_{1/2}$ (s)
P81	3.0	15.6	33	3.0	24	53	3.1	2.9	89	2.9	1.1	161
P81-0.05	3.1	14.8	49	3.0	8.5	76	2.9	2.3	137	2.9	0.56	241
P81-0.10	3.2	10.2	48	3.4	5.9	86	3.1	0.41	162	3.0	0.10	296
P103	3.1	10.2	57	3.2	1.17	98	3.2	0.21	179	3.1	0.06	346
P103-0.05	3.0	6.5	77	3.1	0.58	134	3.1	0.06	245	3.2	0.008	486
P103-0.10	3.1	2.9	102	3.3	0.14	177	3.4	0.009	347	3.4	0.0008	627
P114	3.0	4.8	82	3.1	0.42	154	3.2	0.047	321	3.2	0.0038	546
P114-0.05	3.1	4.1	69	3.2	0.33	137	3.3	0.032	277	3.3	0.0024	493
P114-0.10	3.6	0.55	102	3.6	0.052	177	3.5	0.0069	347	3.4	0.0011	627

Nevertheless, the values of n are in concordance with that published by other authors. For instance, when studying the crystallization of HPB with similar molecular weight to the one used here, Hser and Carr [6] found that n increases from about 2.5–4 as the crystallization temperature goes from 94 to 90 °C. The temperature range over which they measured the crystallization is lower than that used here. In addition, they found that, n slightly decreases with the molecular weight at a given crystallization temperature. In a crystallization study of HPB using dilatometric technique, Alamo et al. [7] found a value of n equal to 3 for most of the studied copolymers; however they mention that in some of the copolymer n can take a value close to 2. The results presented in Table 3 suggest that the characteristics of the crystallization process is not affected by the modification suffered by the molecular structure of copolymers as n takes similar values for all concentrations of peroxide at the different temperatures of crystallization.

The data in Table 3 shows that the crystallization half time increases with the crystallization temperature indicating a decrease of the overall crystallization rate, which is consistent with a crystallization controlled by a nucleation process and a dependence on the under cooling from the equilibrium melting temperature as usually observed for polyethylenes [4,6]. Fig. 5 shows plots of $\ln(1/t_{1/2})$ as a function of crystallization temperature. As expected, the crystallization half-time increased with the crystallization temperature for each polymer [4,6,7]. All the plots in the figure are reasonably linear with essentially the same slope indicating that the temperature coefficients of the crystallization rate of the polymers are similar. There are, however, differences in the crystallization rate that depends on the peroxide concentration

used to modify the polymer. At a given crystallization temperature, the higher the molecular weight of the polymer the slower the crystallization rate. These results are consistent with other data in the literature [6,7].

The influence of the molecular weight on the half crystallization time is given in Fig. 6. The lines in the figure were drawn with proposes of signaling trend. It is interesting to observe in the figure that the data points obtained at a given temperature seem to fall close to the same line. In studies on the crystallization of HPB with concentration of co unit equivalent to the ones used here, Hser and Carr [6] found that the half time goes through a minimum with the molecular weight around 10^4 g/mol, and then increases and eventually reaches a plateau at larger molecular weight. Alamo et al. [7] also found that the crystallization rate of HPB decreases with increasing molecular weight for molecular weight larger than 10^4 g/mol. Thus, based on the augment in the molecular weight induced by the peroxide attack, it was expected that the crystallization rate of the modified polymers displayed lower values than those corresponding to the original polymer. However it is surprising to note that at similar molecular weights, modified polymers show similar crystallization rate to the original HPB as the modification produces high molecular weight species formed by the linkage of between 2 and 4 molecules of the original polymer [28–30]. From previous works it is known that metallocene ethylene copolymer containing long-chain branches, and also star copolymers, crystallize at appreciably slower rate than those copolymers with similar molecular weight but without long branches when they are compared at a given crystallization temperature [13]. Therefore, taking
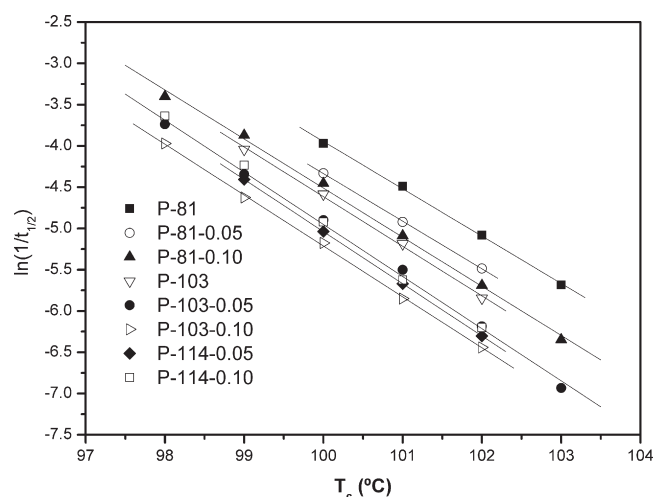
Fig. 5. Plots of $\ln(1/t_{1/2})$ as a function of crystallization temperature.
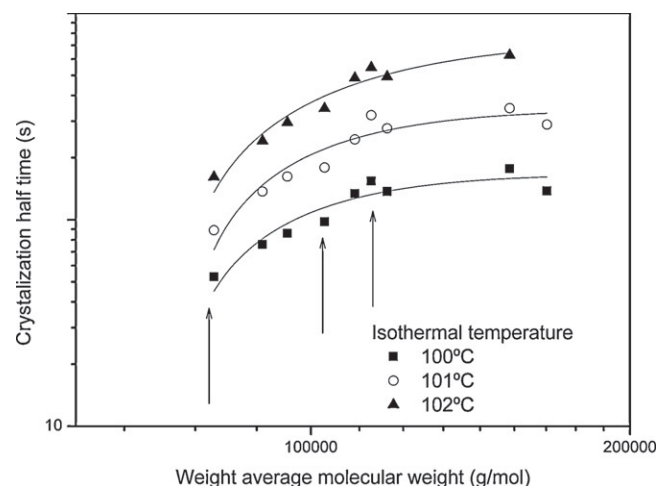
Fig. 6. Half crystallization time ($t_{1/2}$) as a function of weight average molecular weight (Mw).

into account the molecular characteristics of modified polymers, differences between their rate of crystallization and those corresponding to the unmodified polymers when compared at a given molar mass, would be expected. The results indicate that the modification of the polymers with peroxide concentration below the critical point does not generate defect, for instance level of long chain branching and/or type of molecular architectures, into the linear molecular structure of the starting polymer so as to cause noticeable differences between the crystallization rate of modified and unmodified polymers with similar average molecular weights. The results found are consistent with the view that the molecular weight distribution has no appreciable effect on crystallization kinetics of polyethylenes [6]. The crystallization rate of the HPB may result from a balance between the opposing effects induced by the molecular fractions present in the structure. The low molecular weight fractions favor an increment in the crystallization rate while the high molecular weight fractions disadvantage it.

3.2. Non isothermal crystallization

The crystallization of ethylene copolymers in non-isothermal conditions is mainly controlled by the content and distribution of co-monomer unit, which determine the crystallization temperature and crystallinity, while the influence of molecular weight in the process is minimal [11,14–16]. The incorporation of cross-links in the molecular structure of copolymers may influence the crystallization process [21–27]. As an example to demonstrate the effect of the inclusion of crosslinks on the crystallization of HPB, exotherms for P-114 and modified polymers obtained at a cooling rate of 10 °C/min are included in Fig. 7. In concordance with other studies [14–20], the crystallization process of the HPB takes place over a broad temperature range, this is characterized by a major high temperature exotherm followed by a small exotherm extending to lower temperatures. To better visualize the small exotherm, Fig. 7b shows the temperature region of the thermogram on an enlarged scale. The existence of a primary followed by secondary crystallization is a frequent feature observed during the non isothermal crystallization of ethylene copolymers, which is associated with the existence of two crystallization mechanisms occurring in separate temperature ranges [17–20] The mechanism that occurs at high temperature is related to the formation of lamellar crystalline structures, while the low temperature one is tentative ascribed to the formation of secondary crystal-fringed micellar type or to the grows of new lamellas crystal between the lamellae formed during the primary process [17,18]. It can be seen in Fig. 7a that the generation of crosslinking into the molecular structure of the polymers causes the higher temperature exotherm to move slightly towards lower temperatures while the small exotherm does not appreciably change in terms of temperature position or intensity. These changes in the characteristics of the crystallization exotherms were similar for all polymers and studied cooling rates.

From the thermograms, the crystallization peak maxima (T_p) and the crystallization enthalpy (ΔH_c), can be obtained. The enthalpy was measured from the area of the exotherm peak. Table 4 summarizes the parameters for all the samples studied. For each polymer, the temperature, T_p, as well as ΔH_c, gradually decrease by increasing the crystallization rate [14–16]. T_p decreases about 5–6 °C while ΔH_c decreases 5–6% by increasing the cooling rate from 5 to 30 °C/min.

The thermal properties of the HPB are similarly affected by the peroxide attack. The temperature and enthalpy of crystallization did not greatly vary in samples modified with peroxide concentrations lower than the dose of gel. This can be associated to the relatively small difference between the molecular weight of polymers and the low level of imperfections introduced by the peroxide attack [14–16]. On the other hand, the
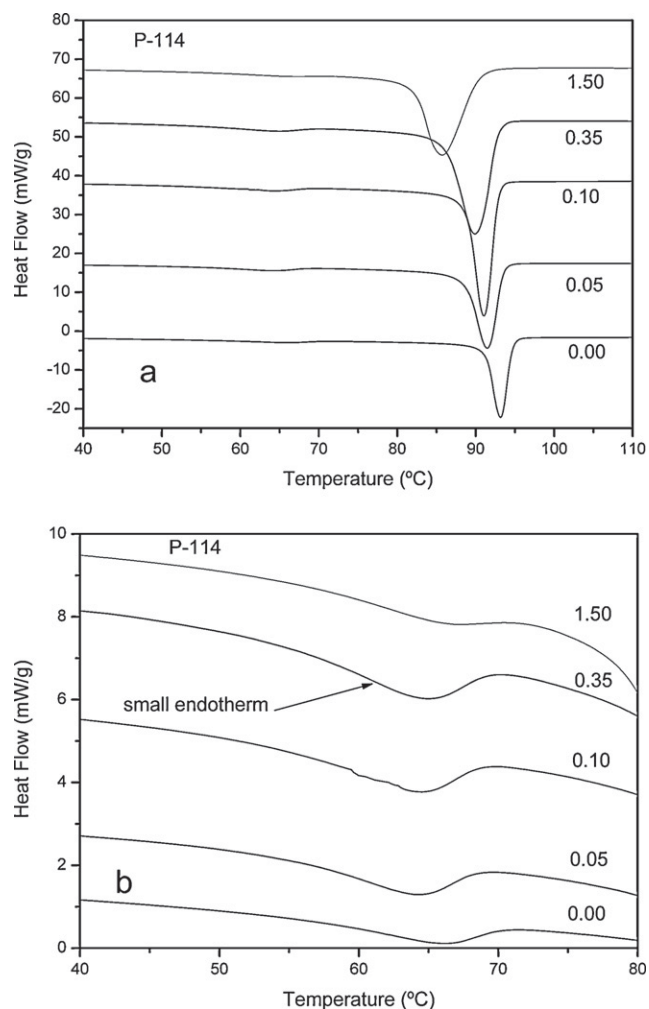

Fig. 7. (a) Crystallization exotherms at a cooling rate of 10 °C/min of P114 and modified polymers with different concentrations of peroxide, (b) temperature region of the thermogram on an enlarged scale.

effect of crosslinking on the thermal properties becomes evident in the samples that have a molecular network. In these cases the crystallization temperature and enthalpy decreased with the peroxide concentration. A proportional relationship exists between crystallization temperature and peroxide concentration. Several authors have observed qualitatively similar changes in the thermal properties of crosslinked polyethylenes [21,26]. In a study on the crystallization of crosslinked low density polyethylene, Nilsson et al. [26] found a decrease of about 10–11 °C in T_c and 6–7% in the crystallinity when the amount of gel reach about 91–95% of the total mass. In a similar study, Kao and Phillips [21] reported a crystallization temperature depression of about 7 °C after the gel amounts about 80% of crosslinked low density polyethylene. The trend in the crystallization temperature and crystallization enthalpy can be associated to the increasing amount of crosslink produces as the peroxide concentration increases, which are excluded from the crystalline region and also to the restriction that they impose to the chain mobility that hinders the crystallization process [24,26].

In order to analyze further the non-isothermal crystallization process, the Avrami formalism was employed. The relative crystallinity was calculated as a function of temperature and transformed to a time scale using the equation:

$$t = \frac{T_i - T}{\phi} \tag{3}$$

Table 4
T_p, ΔH_c, parameters of Avrami equation of modified and original HPB's at different cooling rates. Activation energies of each material are also included.

Sample	ϕ (°C/min)	ΔH_c (J/g)	T_p (°C)	n	k ($\times 10^3$) (s^{-1})	$-E_a$ (kJ/mol)
P81	5	117	95	1.9	17	212
	10	117	94	1.9	22	
	20	114	91	1.6	36	
	30	112	90	1.8	50	
P81-0.05	5	116	95	1.7	15	178
	10	115	94	1.5	26	
	20	111	92	1.3	33	
	30	110	90	1.2	47	
P81-0.1	5	114	95	1.7	14	158
	10	112	93	1.6	24	
	20	110	91	1.4	36	
	30	108	89	1.5	44	
P81-0.5	5	106	91	2.1	15	156
	10	104	89	1.9	23	
	20	102	87	1.7	34	
	30	100	85	1.6	45	
P81-1	5	102	87	1.9	13	142
	10	99	85	1.8	21	
	20	96	82	1.7	33	
	30	95	80	1.7	43	
P114	5	116	94	1.8	26	223
	10	114	93	1.8	42	
	20	111	90	1.8	72	
	30	108	89	1.6	97	
P114-0.05	5	115	93	1.6	20	218
	10	114	91	1.6	32	
	20	111	90	1.5	55	
	30	108	88	1.3	67	
P114-0.1	5	120	92	1.4	22	216
	10	118	91	1.4	38	
	20	110	90	1.4	60	
	30	107	89	1.3	73	
P114-0.35	5	103	92	1.8	16	185
	10	102	90	1.7	27	
	20	101	87	1.4	38	
	30	101	85	1.4	45	
P114-1.5	5	97	88	1.9	11	150
	10	96	86	1.9	19	
	20	96	83	1.9	34	
	30	95	81	1.9	45	

Fig. 8. Relative crystallinity as a function of t for crystallization of (a) original P-81 and (b) P-81 with 1.00 wt% of peroxide.

where T is the temperature at time t, T_i is the initial temperature at time $t = 0$; and ϕ is the cooling rate. As an example, the development of relative degree of crystallinity $X(t)$ as a function of time for P81 and P81-1 at various cooling rates is shown in Fig. 8. The analysis was carried out by fitting the experimental relative crystallinity as a function of time data to the Eq. (3), using a nonlinear multivariable regression program. The Avrami approach was applied to the early stages of crystallization to avoid complications arise from the effects of secondary crystallization process. Thus, relative crystallinity data in the range from 1 to 30% were used in the fitting. Table 4 shows the parameters k and n, obtained from the best fit of the experimental dates as a function of cooling rate. It should be taken into account that in non-isothermal crystallization, the parameters k and n do not have the same physical significance as in isothermal crystallization. Nevertheless, values of k and n have been used to gain further insight into the kinetics of non-isothermal crystallization process of polymers. In Table 4 can be seen that the parameter n takes values from 1.4 to 2, and decrease slightly as the cooling rate increases in all the cases. The value of n does not seem to depend on the peroxide concentration that indicates that the crystallization process of HPB and crosslinked copolymer is similar. In a study on the crystallization of linear low density
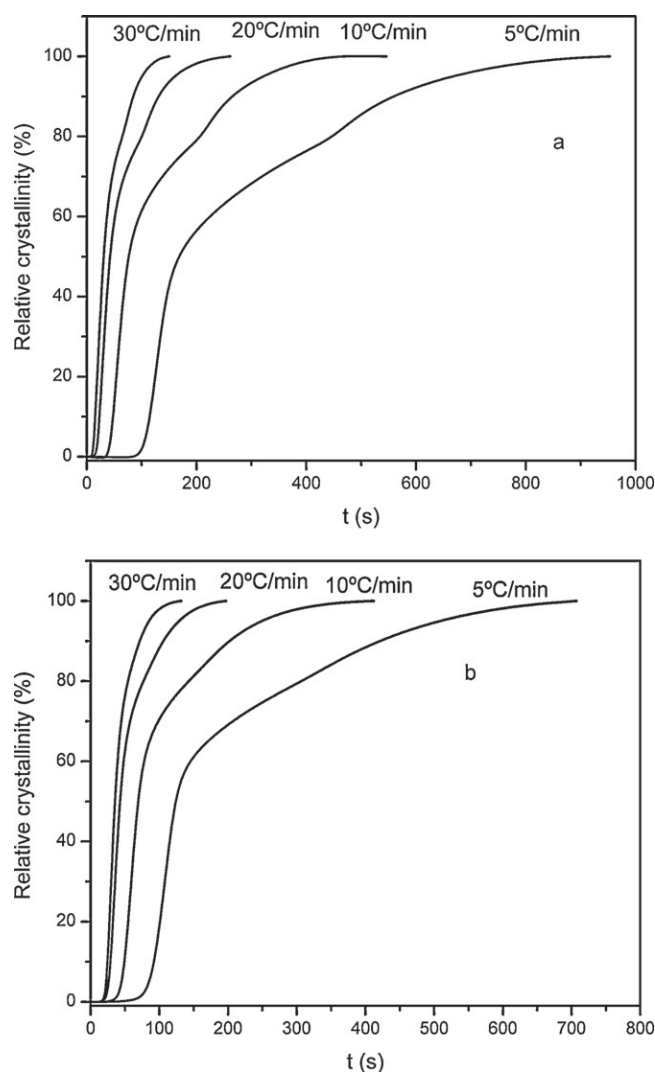
polyethylene crosslinked with silanes, Jiao et al. [25] found values of the parameter n comparable to those presented here.

As it was described above, the crystallization temperature depends on the cooling rate. Thus for extending the analysis of the non-isothermal crystallization process, we have evaluated the effective energy barrier for crystallization. This was obtained by applying the differential isoconversional method of Friedman using the following equation [31]:

$$\ln \frac{dX}{dt} = A - \frac{\Delta E_a}{RT} \qquad (4)$$

where dX/dt is the crystallization rate for a given relative crystallinity, X, A is an arbitrary factor and ΔE_a is the effective energy barrier of the process for a given relative conversion. It should be noted that Eq. (4) is used for the sole purpose of making a qualitative comparison of the crystallization process between the polymers, since the equation was derived assuming a linear relationship between the crystallization rate, the constant of crystallization and the conversion that is not met by the crystallization process of the polymers represented by the Avrami model as it was previously described. The relative crystallinity as a function of time, $X(t)$, was differentiated to obtain the crystallization rate as a function of time. Then, by plotting $\ln(dX/dt)$ measured at various cooling rates against the corresponding inverse temperature for a given

conversion, ΔE_a can be estimated from the slope. It was found that the values of ΔE_a were dependent on the conversion degree, thus with the purpose of comparison ΔE_a was evaluated at a conversion of 30%. The data are presented in Table 4 for some of the polymers. The value of ΔE_a was negative indicating that the rate of crystallization increased with decreasing temperature. It is seen in the table that the activation energy increases with the concentration of peroxide, this is in agreement with the crystallization process restrictions imposed by the molecular cross-linking that increases with the concentration of peroxide.

4. Conclusions

The crystallization behavior of random ethylene–butene copolymers crosslinked by chemical attack with organic peroxide was determined by differential scanning calorimetry.

Under isothermal crystallization conditions, the polymers modified with concentration of peroxide lower than the gel point showed a decrease in the rate of crystallization with the increase in the average molecular weight likewise to that observed for unmodified copolymers. The change introduced in the molecular structure of the copolymers seems to have no effect on the characteristics of the isothermal crystallization process as revealed by analysis of Avrami parameters.

The crystallization rate measured under non-isothermal conditions increased with cooling rate in all the samples. It was found that the enthalpy of crystallization of crosslinked sample measured at constant cooling rate slowly decreased with the peroxide concentration. The effect of crosslinking on the temperature of crystallization was evident in the samples with a molecular network. The crystallization temperature decreased proportionally with the amount of gel. The activation energy for the non isothermal crystallization process decreased with the concentration of peroxide, indicating that the increase in the degree of crosslinking restricts the crystallization process.

Acknowledgements

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