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Polymer 46 (2005) 725–732

polymer

www.elsevier.com/locate/polymer

Modification of model ethylene–butene copolymers using an organic peroxide

Claudio J. Pérez, Enrique M. Vallés, Marcelo D. Failla*

Planta Piloto de Ingeniería Química-PLAPIQUI (UNS-CONICET), Camino "La Carrindanga" Km 7, 8000 Bahía Blanca, Argentina

Received 22 April 2004; received in revised form 22 November 2004; accepted 23 November 2004
Available online 15 December 2004

Abstract

Well-characterized linear ethylene–butene-1 copolymers with polydispersities lower than 1.1 were modified using an organic peroxide with the purpose of assessing the relative importance of chain-linking processes. The copolymers used in this work were obtained by hydrogenation of polybutadienes, which were synthesized by anionic polymerization of butadiene. All the copolymers were modified in the molten state using 2,5-dimethyl-2,5 di(terbutyl peroxy)-hexane with concentrations varying on a ample range. The changes in the molecular structure of the polymers due to the chemical attack of the peroxide were evaluated combining selective solvent extraction and GPC-MALLS techniques. As expected, the critical concentration required for the onset of gelation, C_c, decreases with average molecular mass of the original copolymer. When concentrations of peroxide below C_c are employed, the weight-average molecular mass of the modified copolymers augments and the molecular mass distribution gets wider as the concentration of peroxide added to the copolymer increases. Although, the chain-linking reactions govern the modification process, there is a fraction of molecular chains that suffers scission. The measurable fraction of molecules having molecular mass lower than the original quasi-monodisperse copolymers ranges between 15% and 24% of the total mass when the copolymers were modified with concentrations of peroxide below C_c. Beyond the onset of gelation, the gel amount increases continuously with the peroxide concentration added to the copolymers. At a given peroxide concentration, the amount of gel produced for a given polymer is higher the greater is the initial molecular mass of the modified polymer. The limiting amount of gel was between 90% and 98% of the total mass, which was reached using concentrations 20 times larger than the critical one. The efficiency of the peroxide as cross-linking agent seems to be dependent on the concentration of peroxide.

Keywords: Etylene–butene copolymers; Organic peroxide; Crosslinking

1. Introduction

The modification of polyethylenes (PE) using organic peroxides is a processes widely used to improve their physical and mechanical properties [1–4]. It is usually carried out in the molten state. The advantage of this method with respect to others, such as irradiation, is that it may be carried out with the normal equipment commonly used for the processing of polyolefins, without requiring special installations. At the processing temperatures of the polymer, the homolytic scission of the peroxide O–O bonds generates oxy-radicals. Then, the oxy-radicals extracted hydrogen atom from the saturated chains producing macroradicals, which may follow various chemical reactions that alter the molecular structure of the polymer. In general, the main reaction that takes place is combination of macroradicals that links macromolecules generating cross-linking, long-chain branching, and chain extension [1–9]. This reaction is convenient for improving the polyethylene properties. Nevertheless, there are other competitive reactions, such as chain-scission and formation of unsaturations, that affect the efficiency of the cross-linking and, also, the molecular structure and final properties of the modified polymer [1–4].

The chemical modification of PE initiated by organic peroxides has been investigated in many publications in the open literature. It is well known that when polyethylene undergoes mainly chain-linking the molar mass increases with the concentration of the initiator, until its reach infinitely large values. If the peroxide concentration

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* Corresponding author. Tel.: +54 291 4861700; fax: +54 291 4861600.
E-mail address: mfailla@plapiqui.edu.ar (M.D. Failla).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.11.085

increases even further, a molecular network or gel starts forming. This phenomenon is called gelation. Beyond gelation, the gel grows with the peroxide concentration becoming a large fraction of the total mass. Many of the studies carried out on the modification of PE, analyzed the use of large concentrations of peroxide in order to produce intensive chain-linking so that to obtain a large amount of gel [6–8,10–24]. There are also publications dealing with the modification of PE using concentrations of peroxide below the gel point with the aim of varying its melt properties [5,25–36].

The competition between chain-linking and others secondary reactions determines the evolution of the molecular mass, the critical concentration required to form the first gel and the course of the partitioning between gel and soluble fractions. A combination of various factors has been found to determine the relative importance of those reactions. Among the most important are the molecular structure of the original PE, that is the average molecular mass, the molecular mass distribution and the presence of tertiary carbons and vinyl groups [1,5,8,10,14,19,28–31]. Other factors, such as the type and concentration of peroxide, the reaction conditions and additives, need to be taken into account since they also affect the modification process [7,17,21,36]. Although, the peroxide modification of polyethylene has been extensively studied, the relationship between the cited factors with the relative importance of the main reactions that take place in the modification of PE is not completely understood, nor has yet been quantitatively established. There are studies reaching comparable or contradictory results. For example, there are authors concluding that chain-linking is the main reaction that occurs during the modification [12,17,28]. While, others have suggested that reaction such as chain-scission and creation of carbon double bonds can also play an important role in the process [1,8,32]. It has also been suggested that chain scission is likely to occur in a larger extension in branched polyethylene than in high-density linear polyethylene. However, the efficiency of cross-linking have been found to be high of about 100% in branched polyethylene while lower efficiency, in the range of 20–40%, was observed in linear high density polyethylene [1,10].

The difficulties are, at least in part, due to the fact that most of the studies have been carried out using commercial polymers. These polymers usually have very broad molecular mass distribution and chains with different structures that produce rather heterogeneous materials. The lack of a good characterization of the molecular structure of the initial polymers, together with its complexity, has obscured the analysis and interpretation of the experimental results. Studies dealing with model polymers of homogeneous chemical structure can be an alternative route in trying to establish the competition of the reactions that take place during the modification process. In the past, there have been studies dealing with model substances consisting in low molecular mass analogues to polyethylene [10]. However, to our knowledge, studies involving model polyethylene with homogeneous chemical composition have not been yet presented in the open literature.

Here, we have studied hydrogenated polybutadienes with narrow molecular mass distribution, which are chemically analog to ethylene–(butene-1) copolymers. These polymers were modified using the 2,5-dimethyl-2,5-di(terbutylperoxy)-hexane peroxide as initiator. The purpose of the study was to assess the relative importance of the cross-linking process in that type of polymer. The evolution of molecular mass of the soluble and the gel fraction with the concentration of the peroxide was established. In addition, the molecular mass dependence of the critical concentration required for incipient gel formation was determined. The techniques of size exclusion chromatography combined with light scattering and selective extraction with solvent were used to characterize the molecular structure of the original and modified polymers.

2. Experimental

2.1. Materials

Linear polybutadienes (PB) of different molecular mass were synthesized by anionic polymerization of butadiene under high purity conditions following standard methods [37–39]. The polymerization was carried out in cyclohexane solution, under high vacuum and at room temperature. Tertiary buthyl-lithium was used to initiate the reaction, and isopropanol was the termination reagent. Infrared spectroscopy (IR) was used to determine the double-bond microstructure of the PB's. The IR spectra of the samples, which were obtained using a Nicolet 520FT-IR spectrometer, revealed that about 7% of the butadiene molecules were added to the growing chain of all the PB following a 1,2-addition path.

The resulting polybutadienes were subsequently hydrogenated in solution of toluene using a Wilkinson's catalyst ($RhCl(PPh_3)_3$, which was purchased from Strem Chemicals Inc. The hydrogenation was performed at 90 °C in a Parr reactor, working at 700–psi of hydrogen pressure. The hydrogenation method and conditions followed were similar to the one used by Doi et al. [40]. In order to estimate residual unsaturations, infrared spectra's of the hydrogenated polybutadiene (HPB) were recorded at room temperature on 0.1 mm thick films. Residual unsaturation was monitored from absorption peaks at 910 cm^{-1} and 966 cm^{-1}. The analysis of the IR spectra gave no evidence of any absorption bands that can be associated to double bonds. This confirms that highly saturated hydrocarbon polymers were obtained after hydrogenation. The HPB have a molecular structure chemically similar to a random ethylene–(butene-1) copolymers with a composition of about 20 CH_3/1000 C. This can be inferred from the amount of 1,2-addition of butadiene (~7% mol/mol) measured in the original PB.

Size exclusion chromatography (SEC) was used for the determination of the molecular mass and molecular mass distribution of the hydrogenated polymers (HPB). The Table 1 lists the polymers used in this study and their average molecular mass. The polymers are named HPB#, where # is the number that identifies the weight average molecular mass of the polymer. 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 mass, M_n-LS and M_w-LS, were estimated using the commercial program named ASTRA developed by Wyatt Technology Corp. The average molecular mass, M_n-RI and M_w-RI, of the polymers were also estimated following the universal calibration approach using standards of polystyrene and the corresponding Mark–Houwink constants for polystyrene and polyethylene [41].

2.2. Modification procedure

The 2,5-dimethyl-2,5-di(tert-butyl peroxy)-hexane (DBPH) was used as initiator of the modification process, which was kindly supplied by Akzo Chemical of Argentina. This peroxide has not been so extensively used as others, for instance dicumyl peroxide, in investigation of the chemical crosslinking of PE [5–8,18]. The HPB copolymers in the form of fine powder were impregnated with different amounts of a 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 [7,16,17]. The concentration of peroxide ranged from 0.05% to 4% w/w based on the polymer.

The impregnated HPB's were placed between 3 mm thick steel plates lined with aluminum foils and held apart by a 1 mm thick brass frame. The samples were then compression molded between the hot plates of a hydraulic press for 30 min at 170 °C. Initially, a low pressure was applied to mold the polymer, which was then released. A polymer free of peroxide was tested under those conditions in order to verify if degradation due to ambient oxygen was present. No sign of alteration of the molecular structure was observed.

Table 1
Average molecular weights of the HPB's estimated from SEC-LS

Polymer	M_n-LS (g/mol)	M_w-LS (g/mol)
HPB-29	27,000	29,000
HPB-45	44,000	45,000
HPB-81	80,000	81,000
HPB-114	113,000	114,000
HPB-125	123,000	125,000

The reaction time necessary for assuring a complete reaction was estimated by performing rheological tests following the method used by Bremner et al. [17] for monitoring curing reactions. They consisted in performing a peroxide modification of the HPB between the plates of a rheometer operating in the dynamic mode. The elastic dynamic modulus (G') was continuously measured at 170 °C at a frequency of 10 s^{-1} using samples previously press molded for 5 min at 130 °C. The period of time elapsed until G' of the reacting sample reached a constant value was considered to be the total reaction time. The total reaction time was found to be approximately seven times larger than the halftime of the peroxide, which is approximately 4 min at the reaction temperature according to the technical information given by the supplier. A reaction time of five or six times the halftime of the peroxide at the reaction temperatures is usually considered convenient for assuring an almost total decomposition of the peroxide [1,17].

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 period of 4 h. After each period, the specimens were dried to 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 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 material extracted.

The percentage of gel reported in this work is an average of those obtained from three or four specimens of each one of the modified polymers. The standard deviation of data was about 3%. Manipulation of the samples necessary for carrying out the extraction of soluble and the small mass weighted contributes to such dispersion in the data value. The molecular mass and molecular mass distribution of the soluble fractions of the different modified polymers were determined by SEC. The tests were performed under the conditions used for characterizing the HPB, which were already described.

3. Results and discussion

In the present work five hydrogenated polybutadienes were used with polydispersities lower than 1.1. Their average molecular mass, which are presented in Table 1, range from 29,000 to 125,000 g/mol. The modification of the polymers with the peroxide DBPH is assumed to progress according to the general scheme proposed for the free radical mechanism [7]. The peroxide decomposes when it is exposed to heat, and alkoxy radicals are formed. These radicals can abstract hydrogen atoms from the polymer to form alkyl macroradicals, which may follow different reaction paths. The main reaction is combination, which produces molecular cross-links. However, other reactions are also possible such as chain-scission and unsaturations formation [6,7]. The modification reactions were performed using concentrations of peroxide from 0.02% to 4%. This range allowed to establish the critical concentration for gelation and to determine the evolution of gel with peroxide concentration for all the HPB's.

At concentration below the gel point significant changes in the molecular mass distribution of the original polymers were observed. As an example, Fig. 1 shows the molecular mass distributions of the polymers obtained from the modification of HPB-81 with peroxide concentrations below the gel point. The trace of the original narrow distribution polymer is also included in Fig. 1. Qualitatively similar changes in the molar mass distribution were observed for all the polymers. The Table 2 reports the average molecular mass estimated from SEC-RI and SEC-LS distributions for all the polymers. All the original materials have very narrow Poisson-type molecular mass distributions ($M_w/M_n \leq 1.1$). For this type of starting materials, the width and the shape of the molecular mass distribution become very sensitive to the combined processes of cross-linking and scission. At the high molecular mass side it can be observed the formation of a population of molecules having molar masses about three times larger than the original one. These new species are consequence of the combination of macroradicals reactions that generate molecular linkages. The proportion of such molecules increases as the peroxide concentration increases becoming an important fraction of the total mass of the polymer. On the low molecular side of the distribution, new molecules are present with molar masses lower than the original. They result from a chain-scission process. The increment of the peroxide concentration does not seem to be affecting noticeably the proportions of such molecules. Table 2 also reports the mass fraction of molecules having molar masses lower than those contained in the original polymer. They were estimated analyzing the chromatograms obtained by SEC-LS. Nevertheless, we have to point out that this technique has limitations to accurately measure the species of low molecular mass. For this reason the data reported in Table 2 are only indicative of the scission produced by the peroxide treatment. With this foresight in mind, we may point out that the results suggest that the weight fraction of molecules that have molecular mass lower than those of the original distribution is very similar for all the polymers reaching values between 16% and 24% of the total mass. However, the SEC-LS outcome is accurate enough to clearly confirm that with the peroxide treatment there is a competition between chain-linking and chain scission for this particular system.

After the gel point, only the soluble fraction of modified

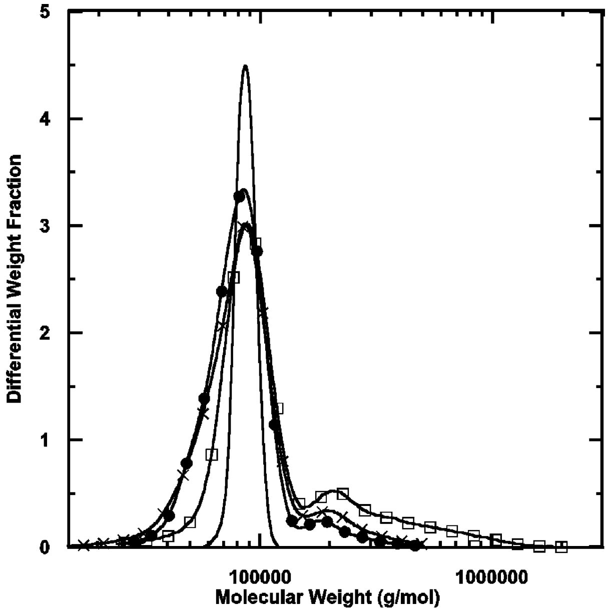

Fig. 1. Differential molecular mass distribution from SEC-LS of the original HPB-81 and the modified polymers obtained using concentration of peroxide below the critical one. Reference: (—), original; (●), 0.05%; (×), 0.1%; (□), 0.2%.

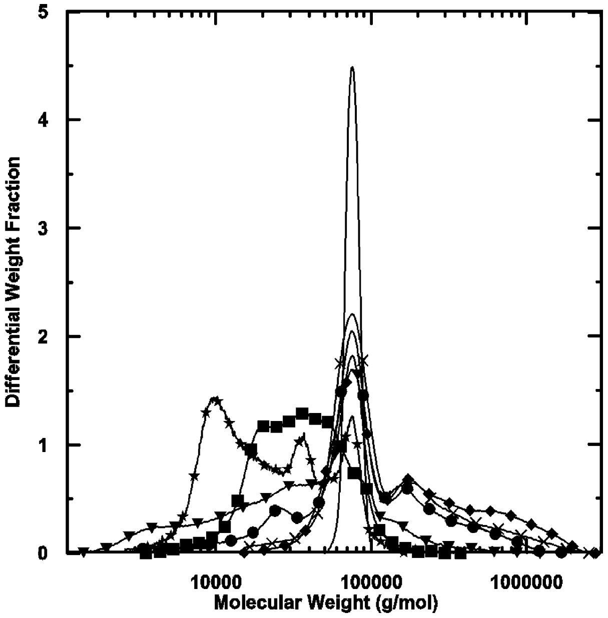

Fig. 2. Differential molecular mass distribution from SEC-LS of the original HPB-81 and the modified polymers obtained using concentration of peroxide above the critical one. Reference: (—), original; (×), 0.23%; (♦) 0.3%, (●), 1%; (5), 2%;(■), 3%; (★),4%.

Table 2
Average molecular weights of the modified HPB's and mass fraction of molecules having molecular weights lower than those corresponding to the original polymer

Sample	Concentration of peroxide (%)	SEC-RI		SEC-LS		[a]Low molecular weight fraction
		M_n-RI	M_w-RI	M_n-LS	M_w-LS	
HPB-29	0	23,000	24,500	27,000	29,000	
	0.3	25,000	33,000	29,000	44,000	0.14
	0.5	24,000	40,000	37,000	55,000	0.18
HPB-45	0	44,300	46,000	44,000	45,000	
	0.2	42,000	50,000	44,000	50,000	0.16
	0.4	53,000	61,000	56,000	63,000	0.18
HPB-81	0	68,000	72,000	80,000	81,500	
	0.05	59,000	67,000	76,000	89,000	0.20
	0.1	64,000	75,000	81,000	94,000	0.20
	0.2	75,000	100,000	89,000	140,000	0.18
HPB-114	0	94,000	99,000	113,000	114,000	
	0.05	95,000	105,000	114,000	118,000	0.24
	0.1	97,000	140,000	119,000	167,000	0.24
HPB-125	0	88,000	98,400	123,000	125,000	
	0.025	94,000	105,000	113,000	128,000	0.21
	0.05	100,000	120,000	110,000	149,000	0.24
	0.1	115,000	129,000	133,000	165,000	0.20

[a] Mass fraction of molecules having molecular mass lower than those corresponding to the original polymer.

material can be studied by SEC. Fig. 2 presents the molecular distribution of the soluble part corresponding to the HPB-81 polymer. The trace of the narrow molecular mass distribution of the parent HPB-81 polymer was included in Fig. 2. Since the gel grows at the expense of the sol by preferentially incorporating the largest molecules, the soluble fraction is enriched in low molecular weight material. For this reason the distributions show broadening only in the low molecular mass region, while the high molecular mass tail decreases. In the cases of the HPB-81 modified with concentrations of peroxide of 3%, the distribution is mainly formed by molecules with molar mass lower than the original. At this level of modification of the HPB-81 the soluble part is just 5% of the specimen mass.

The evolution of the amount of gel, expressed as percentage of the total mass, with the peroxide concentration is presented in Fig. 3. The bars in each data point represent the scattering in the values that were observed. Beyond the gel point the amount of gel increases rapidly with peroxide concentration reaching values larger than 90%. This was especially evident in the polymers with higher initial molecular mass values. For polymers HPB-29 and HPB-45 lower gel levels were obtained because larger concentrations of peroxides were not employed. It can be noticed that the amount of gel developed in the materials depends on the initial molecular weight of the polymer. For a given concentration of peroxide, lower amounts of gel were obtained as the molecular mass of the original polymer diminished.

We have estimated the critical peroxide concentration to reach the gel point, C_c, by extrapolating the available gel fraction data to the x-axis. The values of C_c are presented in Table 3. Due mainly to the lack of a larger amount of data results in the region where the first gel forms we have not been able to estimate C_c with high precision. For this reason we also report in Table 3 the range of peroxide concentration where the gel point should be located. The minimum value of the range was defined as the highest concentration of peroxide used that produces a completely soluble material. The maximum limit of that range was chosen as the lowest concentration at which the gel was detected. The results reported in Table 3 show that the larger is the molecular mass of the initial polymer the lower is the

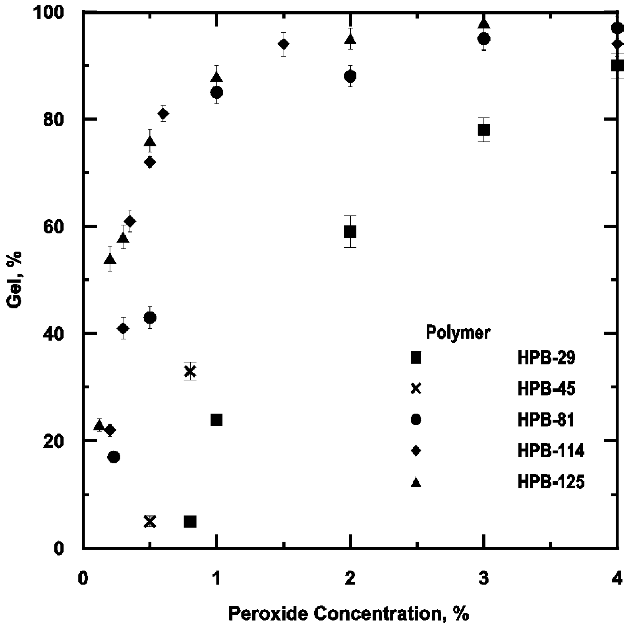

Fig. 3. Proportion of gel (expressed as percentage) of the modified HPB's as a function of the peroxide concentration.

Table 3
Critical concentration of peroxide for gel formation

Polymer	Range of peroxide concentration (%)[a]	Extrapolated (%)[b]	Theory (%)[c]	Efficiency (%)
HPB-29	0.5–0.8	0.70	0.27	38
HPB-45	0.4–0.5	0.42	0.16	38
HPB-81	0.2–0.23	0.20	0.09	45
HPB-114	0.1–0.2	0.12	0.07	58
HPB-125	0.1–0.12	0.10	0.06	60

[a] Range of peroxide concentration where the critical concentration for gel formation is located.

[b] Experimentally determined critical concentration of DBPH, C_c.

[c] Theoretical concentration of peroxide calculated from Flory–Stockmayer relationship, $C_{c,\text{theory}}$

peroxide concentration necessary to generate the first gel. This is expected from theoretical considerations. According to the original statistical theories of cross-linking developed by Flory and Stockmayer [42,43], the critical condition for gel formation, when cross-links are randomly formed into macromolecules of uniform molecular weight, is achieved when

$$\rho_c \approx \frac{1}{Z_w}$$

Here ρ_c is the fraction of units cross-linked and Z_w is the weight-average degree of polymerization. This relationship predicts that the gel point depends on the reciprocal of weight average molecular mass. It has been used for various authors for estimating cross-liking efficiencies in linear polyethylenes, which were exposed to either high-energy radiation or peroxide attack [10,44]. Even though the polymers studied here do not fulfill all the requirements of the theory, we consider that it can provide a reasonable frame of reference for analyzing the results. The polymers have narrow molecular mass distributions, so they may be consider as having closely uniform molecular mass as its mandatory by the theory. However, chain scission is present and not all the carbon units in the molecular chains are equally reactive since the tertiary carbons are more susceptible to chain scission [1].

The experimental results presented in Table 3 were compared with the theoretical expectation $C_{c,\text{theory}}$ assuming a crosslink efficiency of 100% that is two cross-links per peroxide molecule are produced. The experimental values found for $C_{c,\text{theory}}$ are significantly lower than the theoretical ones. This is expected due to the occurrence of chain scission. The crosslinking efficiency presented in Table 3 was estimated from the relationship between the experimental and theoretical values of C_c. It can be observed that the efficiency varies from 30% to 60% when the molecular mass of the polymer increases. The values of the efficiency are in reasonable agreement with those measured by other authors using different types of polyethylene and peroxide. For example Hulse et al. [10] reported efficiency in the range 20–40% when studying the modification of linear polyethylenes with dicumyl peroxide.

From the experimental data reported in Table 3 we may conclude that C_c is not proportional to the reciprocal of the molecular mass. One plausible reason for this is that the either oxy or alkyl radicals may be consumed in secondary reactions producing inert species, which are more abundant when high concentrations of peroxide are employed. The last column in Table 3 shows that when the percentage of peroxide added to the polymer is higher than 0.40% the efficiency of the crosslinking falls to 38%. In contrast, when the percentage of peroxide added to the polymer is less than 0.20% the efficiency raises to approximately 60%.

The cross-linking efficiency is also affected by scission, which is undoubtedly present as revealed by the broadening of the SEC traces in the low molecular mass side of the chromatograms. This process is favored by the presence of tertiary carbons in the polymer chains. Scission may explain part of the differences between the theoretical and experimental values reported in Table 3, but not the lack of proportionality between C_c and the inverse of the molecular mass as discussed in the previous paragraph. The polymers used are characterized by having homogeneous chemical composition and similar concentration of tertiary carbons. Therefore, It would be expected that scission levels would be similar for all the polymers as confirmed by the low molecular mass fractions measured and reported in Table 2.

Fig. 4 presents all the post-gel data plotted as percentage of gel versus the peroxide concentration normalized by the critical concentration for gelation corresponding to each of the original polymers. It can be observed that all the gel data obtained after modifying the HPB with the peroxide describe the same trend. Moreover, they seem to delineate the same curve. This suggests that the peroxi-modification induces similar evolution of the gel amount for all the polymers regardless of their initial molecular mass. If the molecular mass would had a noticeable effect on the peroxide efficiency, a distinctly trend in the evolution of the gel should have been observed among the polymers.

For further analyzing the results we adapted the approximation to the Flory–Stockmayer theory used by Rijke et al. [44] for predicting the evolution of gel with dose of lineal polyethylene fractions that were gamma irradiated. Following their approach we adapted the approximation for the case of using peroxide, which gives the following

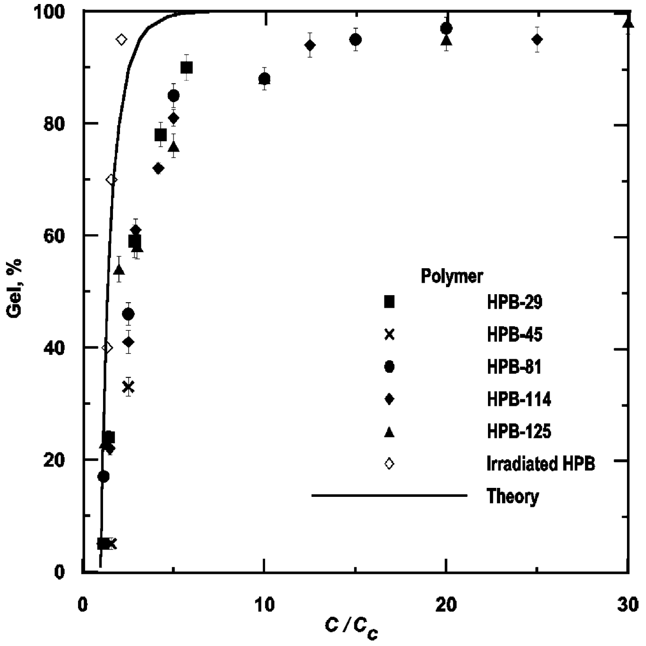

Fig. 4. Proportion of gel (expressed as percentage) of the modified HPB's as a function of the normalized peroxide concentration.

relationship

$$-\frac{\ln w_{\mathrm{s}}}{(1-w_{\mathrm{s}})} \cong \frac{C}{C_{\mathrm{c}}}$$

where, w_{s}, is the soluble fraction, and C and C_{c} is the peroxide concentration and the critical concentration, respectively. The solid line in Fig. 4 represents the theoretical curve. We have also included a set of experimental data extracted from reference [45] that were obtained by modification with gamma radiation of a model HPB ($M_{\mathrm{w}} \sim 50000$ g/mol) with a chemical structure entirely similar to those used here. The polymer crosslinked by radiation adheres well to the theory even though it was reported that a small fraction of chain-scission was present. The results from the peroxide crosslinking reveal that there is a considerable deviation of the experimental data from the theoretical expectation. The deviation is in such a direction that much less gel is produced than the one predictable, which is reasonable to happen if a considerable amount of chain scission is present. Nevertheless, for values of C/C_{c} greater than 15 the gel produced seems to reach asymptotically values very close to 100%. These results indicate that crosslinking reactions predominate and at high peroxide doses, most of the molecules produced by chain scissions are incorporated to the gel.

4. Conclusions

We have investigated the chemical crosslinking of ethylene–1-butene copolymers having narrow molecular weights distributions. The peroxide-initiator employed in this work was 2,5 dimethyl-2,5 di(tert-butyl peroxy) hexane in a wide range of concentrations below and above the critical dose for gelation. Under the modification conditions adopted, It was found that the critical concentration of peroxide necessary to reach the gel point decreases as the initial molecular mass of the crosslinked polymer rises, but does not follows the expected dependency for systems adhering the classic theory of gelation. The peroxide efficiency as estimated from the gel point ranges from 30% to 60%. We found that scission is present in all the modified samples, at levels ranging from 15% and 20%. These results reveal differences with respect of those obtained by gamma irradiation of model copolymers with comparable molecular structure.

Acknowledgements

The authors would like to acknowledge the financial support of the National Research Council of Argentina (CONICET), The Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), and the Universidad Nacional del Sur (UNS).

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