Effect of the Vinyl Concentration on the Structural and Rheological Characteristics of Peroxide-Modified High-Density Polyethylenes

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ABSTRACT: The effect of the hydrogenation of the terminal vinyl groups on the peroxide modification and rheological properties of high-density polyethylene (HDPE) was investigated. The aim of the study was to determine exclusively the effect of the terminal vinyl groups on the peroxide crosslinking and rheological properties of HDPE with one polymer type. This was achieved by hydrogenation of the terminal vinyl groups of a commercial HDPE to obtain an identical material from a structural point of view, which differed only in the nature of the terminal unsaturations, and the comparison of its level of peroxide crosslinking with that of the original polymer. Hydrogenated and unhydrogenated polymer samples were modified at 170°C with different amounts of organic peroxide ranging from 125 to 5000 ppm. Changes in the molecular structure were determined by Fourier transform infrared spectroscopy, size exclusion chromatography, and rheological measurements. Hydrogenation of the terminal groups of the original polymer significantly reduced the rate of modification or crosslinking. The dynamic viscosity and elasticity increased with the level of peroxide modification. Unhydrogenated samples exhibited rapid increases in viscosity and elastic modulus, whereas their hydrogenated counterparts required about 500% of the amount of peroxide needed for the unhydrogenated sample to attain similar structural changes. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1942–1951, 2010

Key words: crosslinking; polyethylene (PE); rheology; viscoelastic properties

INTRODUCTION

Because of its versatility, polyethylene (PE) has become the largest commercially produced polymer. It is used in a wide range of applications as a commodity resin and, in several cases, for more specific uses. However, in some of these applications, improved properties of the PE are required; this thereby compels further modification of its properties to meet the desired quality specification. Crosslinking is often used to achieve this objective. Radical crosslinking with organic peroxide is one major method frequently used in industry to bring about the crosslinking of PE; other method include irradiation and silane crosslinking.[1] Peroxide crosslinking is used for products such as high-performance hot- and cold-water pipes, gas pipes, cable-insulating materials, shrink products, and a host of other products requiring improved properties.

The chemical reactions involved in peroxide crosslinking have been a subject of intensive study over the years. This process is generally believed to involve peroxide homolysis, which yields peroxide radicals that abstract hydrogen atoms from PE and thereby form macroradicals.[1] Crosslinking occurs through the combination of these macroradicals. It was observed from some of these studies that crosslinking efficiency in linear PE depends to a great extent on the concentration of terminal vinyl groups in the parent polymer.[1–8] In our previous studies on the peroxide modification of PE,[9,10] we used high-density polyethylenes (HDPEs) with various concentrations of terminal vinyl groups obtained from different sources. We reported that the higher the vinyl concentration was, the faster the rate of crosslinking and, consequently, the growth of the molecular weight were.

On this premise, the objective of this study was to compare the changes in the molecular structure and

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the rheological behavior induced by peroxide modification on a vinyl-terminated PE with those occurring on the same polymer where terminal vinyl groups were removed by hydrogenation before the peroxide treatment.

EXPERIMENTAL

Materials

The polymer used in this study was HDPE (Alathon 7050) from Du Pont de Nemours (Wilmington, DE) with a weight-average molecular weight (M_w) of 46,700 g/mol and a number-average molecular weight (M_n) of 17,600 g/mol. It was obtained in the form of pellets and converted to a powder form according to the procedure described later. The polymer had a concentration of terminal vinyl groups of 0.033 mol/L, which was measured by Fourier transform infrared (FTIR) spectroscopy.

Chloro tris(triphenyl phosphine) rhodium(I) [$(PPh_3)_3RhCl$; 99%, Strem Chemicals, Newburyport, MA] and triphenyl phosphine (PPh_3; 99%, Aldrich) were used as the catalyst and cocatalyst, respectively, in the hydrogenation reaction. Acetone (99.5%) was obtained from Laboratorios Cicarelli (Argentina) and was used to prepare the peroxide solution. The organic peroxide used in the crosslinking reaction was 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane (DBPH) from Akzo Nobel Química SA. Reagent-grade methanol and xylene were purified by distillation before use in the hydrogenation reaction.

Hydrogenation reaction

The hydrogenation method and conditions that we followed were adapted from the method proposed by Doi et al.[11] The hydrogenation reaction was performed on a solution of the polymer in xylene under a hydrogen pressure of about 700 psi at 120°C. A 2-L high-pressure reactor (Parr Instrument Co., Moline, IL) with temperature, pressure, and stirring control devices used. In a typical hydrogenation reaction, 10 g of HDPE pellets were placed in the reactor, and 1 L of xylene was added. Calculated amounts of the catalyst $(PPh_3)_3RhCl$ (2% w/w) and cocatalyst PPh_3 (6% w/w) based on the weight of the polymer were added. The reactor was first purged with nitrogen (to evacuate air traces inside) and then with hydrogen. Thereafter, the reactor was pressured to 545 psi at room temperature (25°C) with hydrogen. The temperature was raised to 120°C, and the reaction was allowed to run for 24 h with a constant stirring speed (250 rpm). The hydrogenated HDPE powder obtained after 24 h of reaction was precipitated from the xylene solution by the addition of cold and freshly distilled methanol. The precipitate was filtered and washed several times with cold methanol and dried *in vacuo* at ambient temperature.

Similarly, a fine powder of the virgin polymer was obtained by the dissolution of 10 g of pellets in 1 L of xylene at 120°C under an inert atmosphere with constant stirring with a pressure reactor as described previously. The experimental procedure used to obtain this powder is described next. Xylene and the virgin polymer pellets were placed inside the reactor. Then, a smooth nitrogen flow was used for 15 min to evacuate traces of air inside. After this, the reactor was pressured at 50 psi with nitrogen at room temperature (25°C) to prevent possible oxidation reactions over the pellets during heating. The temperature was raised to 120°C, and the solution inside was heated for about 3 h at a constant stirring speed (250 rpm). The polymer powder was then precipitated by the addition of cold methanol to the xylene solution. It was filtered and washed several times with cold methanol and dried *in vacuo* at room temperature.

Modification reaction

A known weight of the polymer powder was impregnated with the calculated amount of the solution of the peroxide in acetone that would furnish the predetermined peroxide concentration in the polymer sample upon the evaporation of the solvent. The peroxide concentration that we used varied from 125 to 5000 ppm. The samples obtained by this procedure were named with the codes PE-# and HPE-#, where PE and HPE indicate the original polyethylene and the hydrogenated polyethylene, respectively, and # is the concentration of peroxide (ppm).

The crosslinking reaction was performed by the compression molding of each sample at 170°C and 50 bar for 5 min between the plates of a hydraulic press with the polymer sandwiched between two brass plates. Thereafter, the pressure was released, and the sample was left between the plates of the hydraulic press for an additional 15 min at 170°C.

Molecular characterization

FTIR analyses of the thin films of the samples were performed with an IR spectrophotometer (Nicolet, Madison, WI; model 520) operating at a resolution of 4 cm^{-1}. The films were prepared by compression molding at 150°C with a hydraulic press with thermostatically controlled platens. The samples were molded between 5-mm-thick aluminum plates lined with Mylar film and held apart by 0.1-mm-thick aluminum spacers. The molten samples within their metal plates were removed from the hot press and allowed to cool slowly to room temperature. To

TABLE I
M_n, M_w, and η_0 Values of the Polymers

Polymer	M_n (Da)	M_w (Da)	η_0 at 170°C (Pa s)
PE	17,600	46,700	720
PE-125			2,200
PE-250	21,600	55,500	4,250
PE-500	26,100	78,700	105,000[a]
HPE	14,700	47,000	655
HPE-125			765
HPE-250			940
HPE-500	19,900	48,100	1,200
HPE-1000	19,600	52,100	3,300[a]
HPE-4000	20,400	61,400	12,200[a]
HPE-5000	—[b]	—[b]	52,000[a]

[a] As the value of η_0 was not reached in the experiment, the value of η' at $\omega = 0.1\ s^{-1}$ is indicated.
[b] SEC measurements were not performed because of the proximity to the gel point.

compensate for the differences between the films thickness of the specimens, the recorded FTIR spectra were normalized with the absorbance of the peak at 2019 cm^{-1}, a combination band associated with the twisting of CH_2 groups that has been used by different authors as an internal thickness band for PE because it can be regarded as unaffected by small changes in the polymer structure.[12–15]

M_w and the molecular weight distribution (MWD) values were obtained with a Waters 150 CVgel permeation chromatography instrument equipped with a set of three 20-μm PLgel mixed-A columns (Polymer Labs, Amherst, MA). The solvent used in these experiments was 1,2,4-trichlorobenzene at 135°C at a flow rate of 1 mL/min. M_n and M_w of the polymers were obtained by size exclusion chromatography (SEC) calibration with narrow MWD polystyrene standards (Pressure Chemical Corp. and Polymer Labs), M_w ranging from 580 to 11.6×10^6, and polydispersities lower than 1.19. Benoit universal calibration[16] was used, and the Mark–Houwink constants (K and α) for PE and polystyrene in 1,2,4-trichlorobenzene at 135°C were obtained from the literature.[17] The adopted values were $K = 1.21 \times 10^{-4}$ dL/g and $\alpha = 0.707$ for polystyrene and $K = 4.06 \times 10^{-4}$ dL/g and $\alpha = 0.725$ for PE. The samples were injected several times at concentrations between 1 and 3 mg/mL, and average molecular weights were obtained as the mean value among them. The obtained values of M_n and M_w are shown in Table I.

Rheological studies of the samples were carried out with a rotational rheometer (Dynamic Analyzer RD II, Rheometrics, Inc., Piscataway, NJ) with parallel plates 25 mm in diameter. The frequency ranged from 0.1 to 500 s^{-1}, and the temperature ranged between 150 and 190°C. All of the tests were performed under a nitrogen atmosphere to prevent possible oxidative degradation. At each temperature, strain sweep runs were first carried out to determine the linear viscoelastic region to perform the test experiments. The elastic modulus as a function of the angular frequency [$G'(\omega)$] and viscous modulus as a function of the angular frequency [$G''(\omega)$] of each sample were measured in small-amplitude oscillatory shear flow. The dynamic viscosity as a function of the angular frequency [$\eta'(\omega) = G''/\omega$, where G'' is the viscous modulus and ω is the angular frequency], the phase angle (δ), the complex modulus [$G^* = (G'^2 + G''^2)^{1/2}$, where G' is the elastic modulus], and the reduced complex modulus [G^*/G_N^0, where G_N^0 is the rubbery plateau modulus (2.0 MPa for PE)] were calculated from the rheological data that we obtained.

RESULTS AND DISCUSSION

Figure 1 shows the region of interest in the FTIR spectra of unhydrogenated PE, HPE, and some of the polymers obtained after modification with the peroxide. To compensate for the differences between the film thicknesses of the specimens, the spectra were normalized with the absorbance of an internal peak at 2019 cm^{-1}, which was associated with CH_2 groups. To visualize the differences between the spectra, they were slightly shifted along the absorbance axis. The analysis of the spectra of the original PE through the absorbance bands centered at 908 and 889 cm^{-1} indicated that the unsaturated groups present were vinyl and vinylidene, respectively. The signal associated with the vinyl groups was completely absent in the spectra marked as HPE, which corresponded to the hydrogenated polymer. This

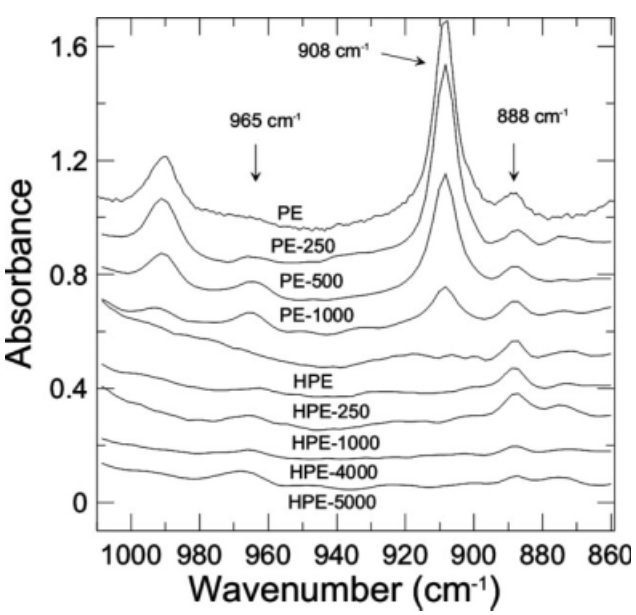

Figure 1 FTIR spectra of unhydrogenated PE, HPE, and modified samples of HDPE with different amounts of peroxide.

indicated that the vinyl groups were successfully hydrogenated. A further comparison of the spectra of the hydrogenated and unhydrogenated PEs revealed that the vinylidene groups were not affected by the hydrogenation procedure adopted here; we deducted this by comparing the absorbance of the peak ascribed to the chemical group that was centered at 889 cm^{-1}.

The spectra corresponding to the peroxide-modified PE showed a decline in the absorbance of the 908-cm^{-1} band with the concentration of peroxide; this indicated a reduction in the concentration of vinyl groups. This observation was consistent with our previously reported results for the peroxide crosslinking of the same unhydrogenated polymer.[9,10] It also went along with several results already present in various reports, where it has been described that the vinyl functionality plays a significant role in the peroxide modification of PE and affects the crosslinking efficiency.[1–8] For instance, Peacock[4] reported exponential decay of the concentration of terminal vinyl groups in linear PE with increasing concentration of dicumyl peroxide. Also reported has been an exponential reduction in the concentration of vinyl groups when poly(ethylene-*co*-1,9-decadiene) was crosslinked with dicumyl peroxide.[7,8]

In a previous study, where the concentration of vinyl group was measured by the analysis of the FTIR spectra of samples of PE modified under similar conditions, we found that the fraction of vinyl groups consumed was proportional to the square root of the peroxide concentration.[9] Similar relationships between vinyl groups and peroxide concentrations have been reported by other authors.[7,8] These results induced Smedberg et al.[7] to propose that the vinyl groups were consumed by a reaction similar to that generated during the polymerization between a vinyl-containing monomer and an active radical initiated with the decomposition of peroxide molecules. These data, together with those obtained in our previous work, are shown on Figure 2. The new data points fell well in the range of the previous experiments but did not exhibit such a good fit with the dotted straight line obtained from the regression of the preceding experiments. This may have been due to the fact that, in this case, we worked with smaller samples (from 4 to 5 g) to obtain each modified polymer to avoid handling large volumes of solvents for the preparation and hydrogenation of the original PE. The difficulty arose from the necessity to measure accurately very small volumes of a dilute peroxide solution to dose the polymer with the desired amount of peroxide in a concentration range where there existed a very rapid decay of vinyl groups in the polymer.

A further analysis of the spectra, presented in Figure 1, indicated that the modification of HPE and

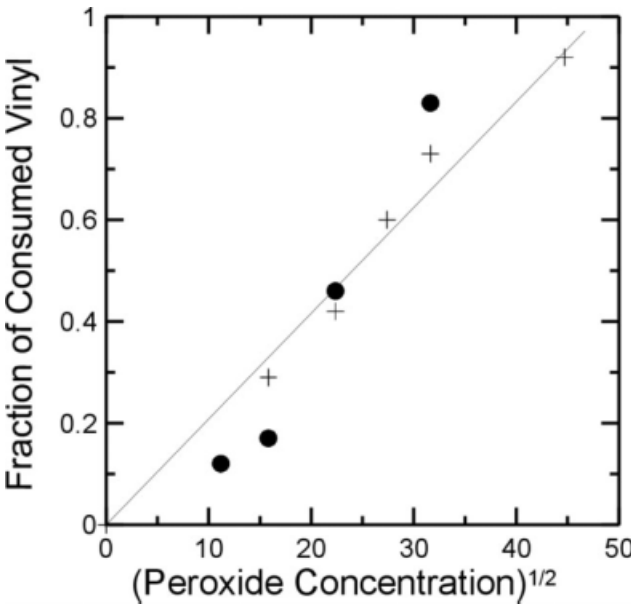

Figure 2 Fraction of consumed vinyl groups as a function of the square root of the peroxide molar concentration for HDPE: (●) this work and (+) ref. 9.

nonhydrogenated PE resulted in the production of *trans*-vinylene groups, as could deduced from the development of its characteristic band centered at 965 cm^{-1}. The concentration of this type of unsaturation was found to increase with peroxide concentration for both the PE and HPE polymers. The formation of this type of unsaturation has generated some controversial opinions about the mechanism of crosslinking formation. On one hand, Bremmer et al.[6] suggested that the dominant mechanisms of molecular linking was the coupling reaction between allylic radicals, formed by the abstraction of an allylic hydrogen by oxy radicals and another macroradical. In this interpretation, the terminal vinyl groups are transformed into *trans*-vinylenes. On the other hand, Smedberg et al.[7] stated that the formation of trans unsaturations resulted independently of the amount of vinyl groups consumed and that this type of group could be formed because of a cage effect of the peroxide.

Comparing the evolution of the intensity of the band associated with the trans group in Figure 1, we can make two comments. In the case of the modified polymer obtained from PE, as the concentration of peroxide increased, the increment of the intensity of the trans band was not proportional to the reduction in the intensity of the vinyl group. The other observation was that the increment measured of the intensity of this band with rising peroxide concentration was larger for the polymers obtained from the PE having vinyl terminal groups than for those polymers obtained by the modification of the HPE. For instance, the absorbance of the trans band

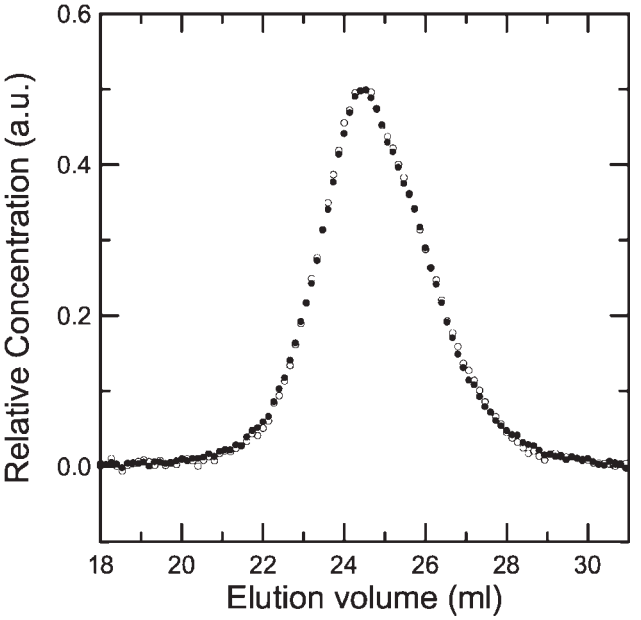

Figure 3 Normalized SEC chromatograms of (●) unhydrogenated and (○) hydrogenated HDPE.

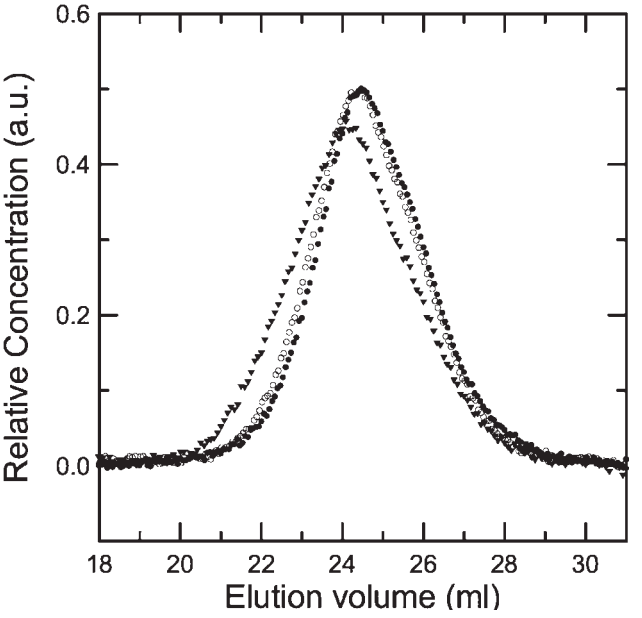

Figure 4 Normalized SEC chromatograms of unhydrogenated HDPE samples modified with different amounts of peroxide: (●) neat unhydrogenated HDPE, (○) PE-250, and (▼) PE-500.

corresponding to the polymer obtained from the modification of PE with 1000-ppm peroxide was comparable to that of the polymer obtained from the modification of HPE with 5000-ppm peroxide. These observations suggest that both of the mechanisms mentioned previously may have been operative in the system under study.

A further comment can be drawn by analysis of the spectra of the modified HPE polymer in Figure 1 is that there was no indication that terminal unsaturation, vinyl or vinylidene, were formed in the range of peroxide concentration used. The formation of those terminal groups has been taken as evidence of the occurrence of chain scission.[6] On the contrary, there existed a slight tendency for a reduction in the concentration of the vinylidene groups for the hydrogenated polymer modified with the highest peroxide concentrations, as could be inferred from the decreasing intensity of the 889-cm^{-1} absorption band. A decrease in the concentration of vinylidene groups with peroxide concentration was reported by Smedberg et al.[7] in a study of crosslinking reactions in unsaturated PEs. The results presented in Figure 1, together with those corresponding to the SEC chromatograms discussed later, did not show evidence that molecular scission took place in a detectable amount in the system studied.

Figure 3 shows the superimposed normalized SEC chromatograms of the original vinyl-terminated PE and that of the polymer obtained after hydrogenation of the vinyl groups. No difference in MWD was observed between these polymers. This confirmed the absence of chain scission during the hydrogenation process. The M_w values determined from the SEC measurements for the unhydrogenated and hydrogenated samples were found to be 46,700 and 47,000 g/mol, respectively. These values were equivalent within limits of experimental error. The normalized SEC chromatograms of the modified samples are shown in Figure 4 (unhydrogenated) and Figure 5 (hydrogenated). As shown in Figure 4, the

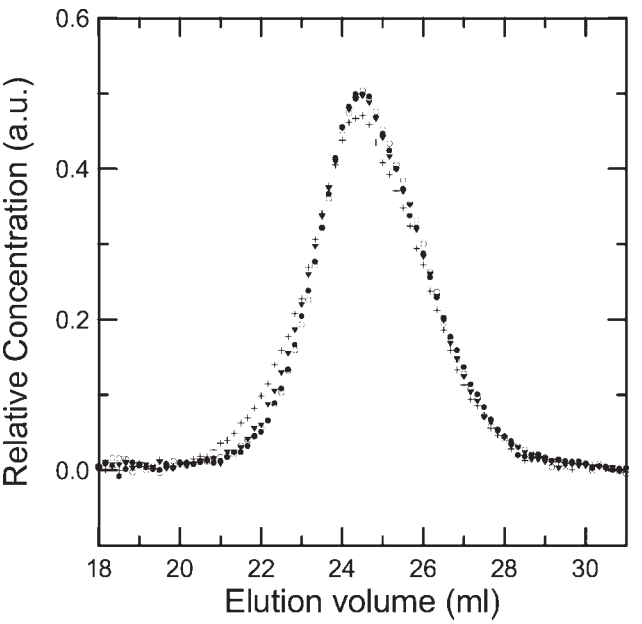

Figure 5 Normalized multi-angle laser light scattering chromatograms of hydrogenated HDPE samples modified with different amounts of peroxide: (●) neat hydrogenated HDPE, (○) HPE-500, (▼) HPE-1000, and (+) HPE-4000.

sample modified with 500-ppm peroxide showed a clear displacement of the entire chromatogram toward lower elution volumes, which implied a significant increment of the molecular weight as a consequence of the crosslinking process induced by the peroxide. The fact that the entire chromatogram curve was displaced by the peroxide modification was explained as being a consequence that the concentration of vinyl groups on the original PE was about one per polymer molecule.[9,10] Because the reactivity of the terminal vinyl groups was high and virtually every molecule of the original PE had a terminal vinyl group, all of the virgin PE molecules had about the same probability of reaction through these groups with the macroradicals generated by the decomposition of the peroxide. As the terminal vinyl groups reacted, the chains were linked by their vinyl-containing ends to the main chain of the existing macroradicals to form long branches that contributed significantly to shift the whole distribution toward higher molecular weights.

The chromatograms corresponding to the polymers obtained from the modification of HPE are shown in Figure 5. The chromatogram for the HPE-5000 polymer was not included in the figure because evidence of the partial solubility of the polymer was found. A clear displacement of the elution curve with respect to the original polymer was only observed for the sample modified with 4000-ppm peroxide. Even with this amount of DBPH, the observed changes were not as significant as those obtained on the vinyl-ended PE with 500-ppm peroxide. This emphasized the strong influence that the presence of vinyl terminal groups had on the efficiency of the peroxide crosslinking.

Another difference was also evident from the comparison of the chromatograms obtained from the modified PE and HPE. Although the peroxide treatment of the vinyl-terminated PE produced a complete displacement of the SEC curves as explained, the same procedure on the hydrogenated counterpart brought on a different pattern of behavior. In the absence of terminal vinyl groups, the crosslinking reaction could only proceed by a combination of pairs of macroradicals that were formed by attack of the decomposing peroxide units, which abstracted hydrogen atoms from the PE chains. The hydrogen abstraction could take place on any of the repeated units that composed the PE chains. For this reason, higher molecular weight chains containing more monomer units had a higher probability to be transformed into macroradicals and to react to form higher molecular weight species. This mechanism of reaction induced a preferential displacement of the higher molecular weight side of the chromatograms toward lower elution volumes, as was clearly appreciated in the HPE-4000 chromatogram reported in Figure 5.

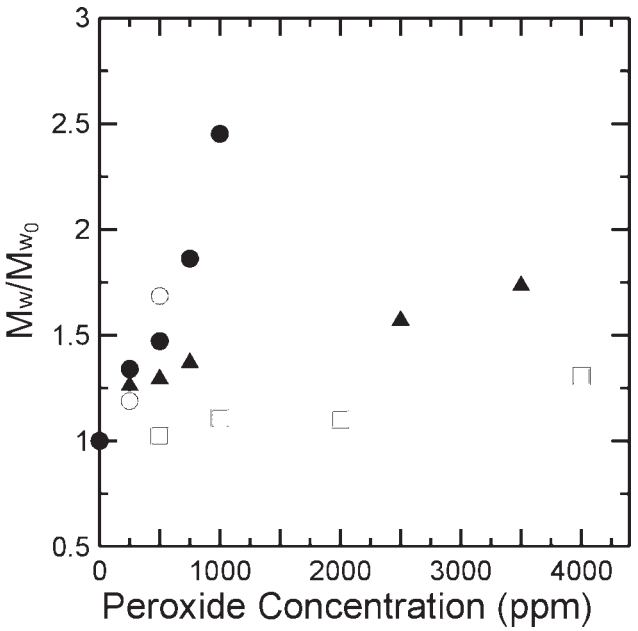

Figure 6 M_w/M_{w0} as a function of the peroxide concentration: (○) PE (this work), (●) PE (ref. 9), (□) HPE (this work), and (▲) PE with a lower concentration of vinyl groups (ref. 9).

The data presented in Figure 6 highlight the effect of the concentration of terminal vinyl groups on the evolution of the molecular weight of the modified polymers. The plot shows the evolution of the relative weight-average molecular weight (M_w/M_{w0}, where M_{w0} is the average molecular weight of the initial PE) as a function of the peroxide concentration. In the figure, the solid symbols correspond to data results taken from our previous study. Thus, solid circles represent previous data, whereas open circles represent the results for the peroxide modification of the original PE in this study. Open squares describe the evolution of the molecular weight of the modified HPE. A stronger increment in the molecular weight of the polymers obtained by modification of the originally vinyl-terminated PE was clearly observed with respect to those obtained from the corresponding hydrogenated polymer. Another set of results (solid triangles) corresponding to the peroxide modification of a PE of an equivalent molecular weight ($M_w = 55{,}000$) with a concentration of terminal vinyl groups of 0.0043 mol/L is also shown in the figure. These are also results from a previous study.[9] In this case, the concentration of terminal vinyl groups was about 10 times lower than that of the original PE considered in this study. The evolution of the molecular weight with the applied concentration of peroxide was between the data for PE and HPE; this confirmed the relationship that

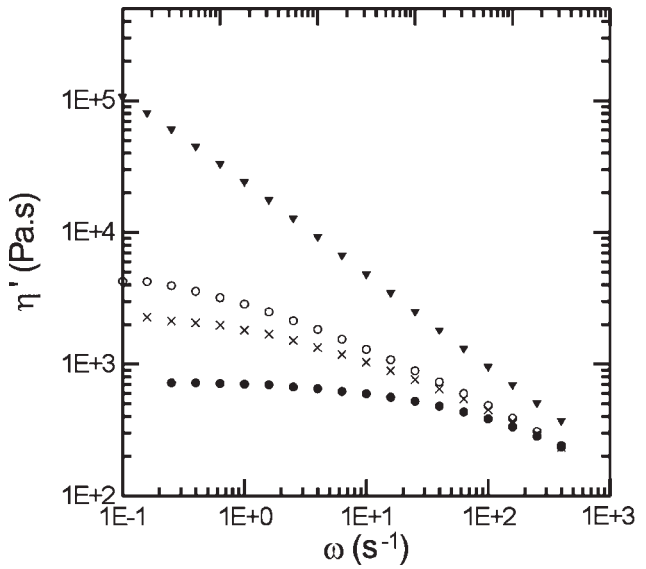

Figure 7 ω dependence of η′ for unhydrogenated HDPE samples modified with different amounts of peroxide at 170°C: (●) neat unhydrogenated HDPE, (×) PE-125, (○) PE-250, and (▼) PE-500.

existed amid the concentration of vinyl groups and the reactivity with the peroxide modifiers.

We now turn to the rheological behavior of the modified PEs. Figure 7 shows the evolution of the dynamic viscosity (η′) with frequency at 170°C of the original PE containing vinyl terminal groups and those of the peroxide-modified samples with increasing concentrations of DBPH. In the low-frequency region of the η′ plots, a rapid growth of η′ with increasing concentration of peroxide was observed, in agreement with the observations of other authors.[9,10,18–23] This was a consequence of the crosslinking reactions that induced the formation of long branches on the linear chains of the original polymer. As it is well known, the presence of long-chain branches considerably enlarge the viscosity at low shear rates because of the dramatic increase in relaxation times induced by the topological constraints introduced by the branches.[9,10] At higher shear rates, η′ of the modified polymers falls to levels that are comparable to those of the original linear polymer. This is also a characteristic behavior of branched polymers.

The results obtained with the peroxide modification of HPE are shown in Figure 8. First, the η′ results of the virgin HPE and PE polymers superimposed on the whole range of frequencies covered by our experiments. The entirely similar rheological behavior of both samples in an experiment that is known to be very sensitive to molecular weight and chain branching on the lower frequency range confirmed that no changes in the molecular structure were produced by the hydrogenation procedure, and this corroborated the similarities observed with the SEC characterization that provided undistinguishable traces among the chromatograms corresponding to both materials.

When the η′ results attained with the peroxide-modified HPE are compared with those shown in Figure 7, it is immediately evident that the η′ curves exhibited considerably milder changes in the low-frequency region than those observed for the modified PE. Table I shows the zero-shear-rate viscosity (η_0; when attained) of the polymers studied. In the case of the samples where the η_0 value could not be calculated from the rheological measurements, the η′ values at $\omega = 0.1\ s^{-1}$ are indicated. As an example, the values of η′ at $\omega = 0.1\ s^{-1}$, measured for the vinyl-terminated PE modified with 250-ppm DBPH (PE-250) were not attained for HPE with the incorporation of 1000-ppm DBPH (HPE-1000). Furthermore, the measured value of η′ = 105,000 Pa s at $\omega = 0.1\ s^{-1}$ obtained by the modification of original PE with 500-ppm DBPH was not reached for the HPE polymer, even when it was modified with 5000-ppm peroxide; that is, there was an order of magnitude difference in the peroxide dose.

The experimental changes in G' at 170°C for the virgin PE and HPE when these materials were modified with increasing doses of DBPH are illustrated in Figures 9 and 10, respectively. For the samples modified with lower doses of peroxide (<250 ppm for the original polymer and under 1000 ppm for its hydrogenated counterpart), an immediate shift in the terminal zone toward lower frequencies was observed, but only mild changes appeared in the transition to the rubbery plateau. This was a clear

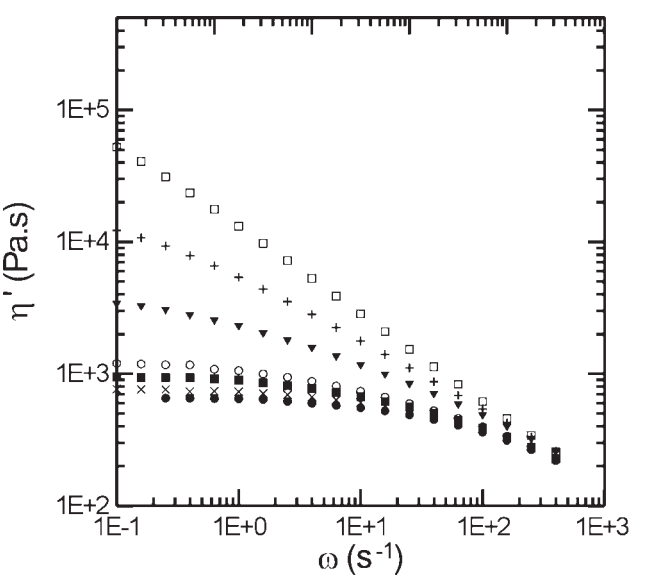

Figure 8 ω dependence of η′ for hydrogenated HDPE samples modified with different amounts of peroxide at 170°C: (●) neat hydrogenated HDPE, (×) HPE-125, (■) HPE-250, (○) HPE-500, (▼) HPE-1000, (+) HPE-4000, and (□) HPE-5000.

indication that the formation of long-chain branches was the main structural change induced in the first stages of the crosslinking process. Long-chain branching affects long-time relaxations but does not alter significantly the local behavior of short segments of polymer chains, which are the ones that dominate the viscoelastic performance at high frequencies. At higher concentration of peroxides, more significant changes were observed that affected the viscoelastic response in the whole range of frequencies comprised on the experimental window covered by our experiments. By comparison of the results shown in Figure 10 with those of Figure 9, it was again evident that much larger alterations in G' were obtained by modification of the vinyl-terminated PE with small peroxide doses than by application of the same procedure to its hydrogenated counterpart.

Recently, Trinkle et al.[24] proposed that reduced Van Gurp–Palmen plots can be useful to characterize the topology of branched polymers according to the location of the so-called characteristic point (P_c), which they defined as a more or less developed bump between the location of G_N^0 and the plateau at $\delta = 90°$. This point corresponds to the intersection of the two tangent lines enclosing the bump, which are easily defined for model star polymers. To characterize the rheological behavior of our modified polymers, we constructed those plots to typify the progress of the crosslinking process for the rheological data under discussion. Figures 11 and 12 show the corresponding results for the original and peroxide-modified PE and HPE, respectively. To construct these plots, the value of G_N^0 for PE was taken to be 2.0 MPa.[25]

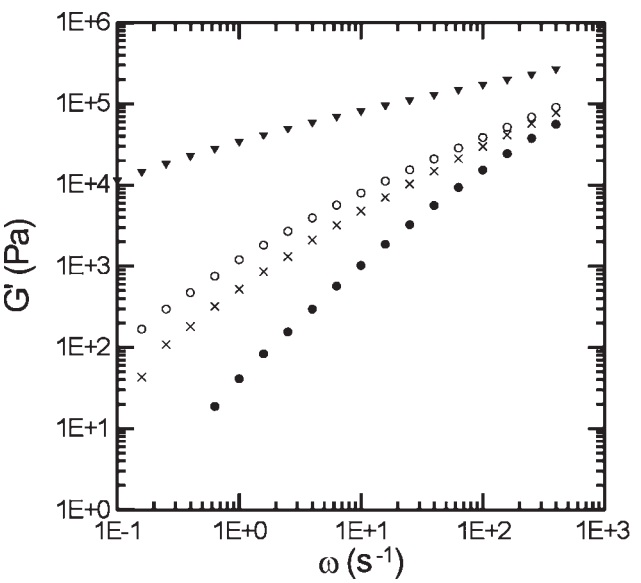

Figure 9 ω dependence of G' for unhydrogenated HDPE samples modified with different amounts of peroxide at 170°C: (●) neat unhydrogenated HDPE, (×) PE-125, (○) PE-250, and (▼) PE-500.

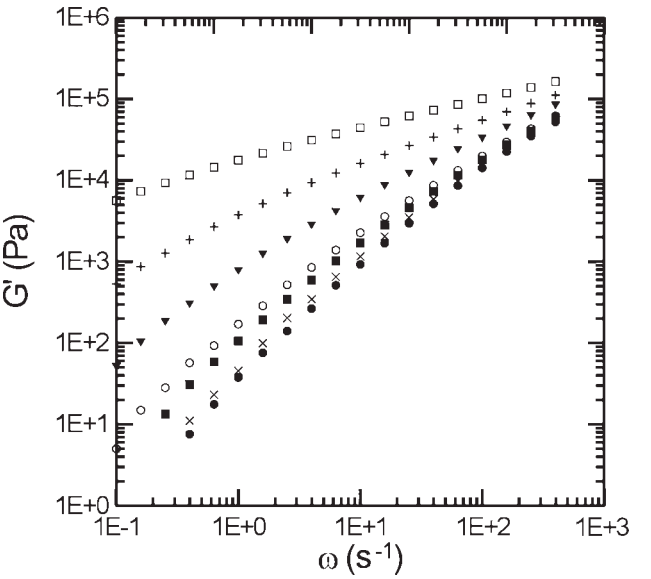

Figure 10 ω dependence of $G'(\omega)$ for hydrogenated HDPE samples modified with different amounts of peroxide at 170°C: (●) neat hydrogenated HDPE, (×) HPE-125, (■) HPE-250, (○) HPE-500, (▼) HPE-1000, (+) HPE-4000, and (□) HPE-5000.

In our case, the position of P_c was not as well developed as in the case of the model star polymers studied by Trinkle et al.;[24] for this reason, we located P_c for each set of data at the inflection point defined

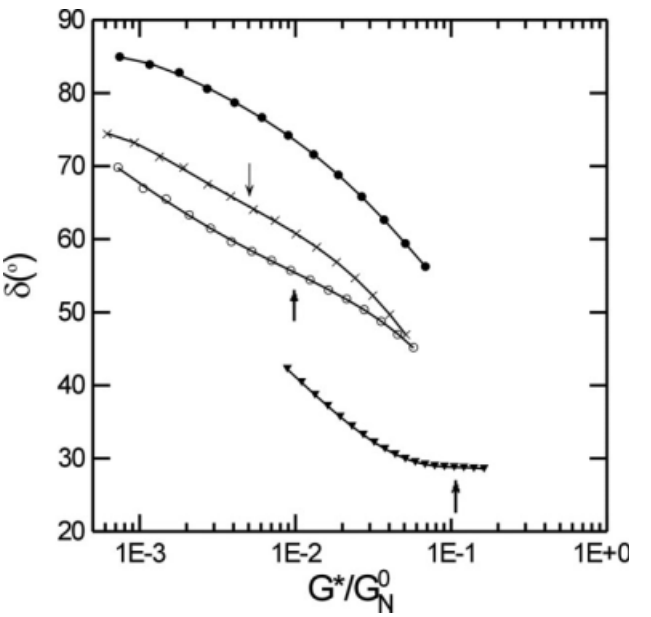

Figure 11 Van Gurp–Palmen plot of the original PE and modified unhydrogenated PE: (●) neat unhydrogenated HDPE, (×) PE-125, (○) PE-250, and (▼) PE-500. The continuous lines correspond to fitting polynomials employed to locate P_c, which is indicated by arrows, as explained in the text.

by the experimental points of the peroxide-modified polymers on the δ versus G^*/G^0_N plots. In both cases, significant deviations of the evolution of δ from the curves corresponding to the initially linear PE and HPE polymers were observed. Those deviations increased with the amount of peroxide used to change the molecular structure of the original polymers. At equivalent amounts of peroxide, the changes were more significant on the PE containing terminal vinyl groups. P_c was difficult to locate under the mild modifying conditions obtained with DBPH doses below 500 ppm for the HPE, but it could be determined for the modified PE and for concentrations exceeding that dose in the HPE. To identify unambiguously the location of the critical point at the turnover of the curvature of each of the trajectories described by the experimental data, we fitted the evolution of those data to a fifth-degree polynomial, as shown in Figures 11 and 12, and looked for the location of the inflection point on those curves. The fitting procedure with fifth-degree polynomials was always excellent, with regression coefficients ranging from 0.9996 to 1. The position of the critical point was then obtained at the location where the second derivative of the obtained polynomials changed sign from positive to negative. The arrows in Figures 11 and 12 indicate the location of P_c for each of the curves were a zero second derivative was present. The positions of P_c obtained for each DBPH dose from Figures 11 and 12 were then plotted in the topology map proposed by Trinkle et al.[24] in Figure 13. All the resulting points were positioned in the region corresponding to mixtures of linear and highly branched chains. A straight line with a slope of −30° per decade fit all the critical points from the modified PE and HPE. This suggested that no significant differences existed in the structure of the branched molecules originating from both polymers. With increasing doses of DBPH, the position of the critical points moved as indicated by the arrow. The evolution of the critical points evolved from the region corresponding to light mixtures of branched molecules with linear PE chains toward lower values of δ, trespassing the boundaries of the zone that corresponded to the highly entangled polymers in the case of the highest doses. On the basis of these observations, it seemed that the modified polymers behaved like homogeneous mixtures of linear molecules, which were those not affected by the peroxide radicals, with branched molecules that increased in complexity and concentration as the crosslinking process became more and more important.

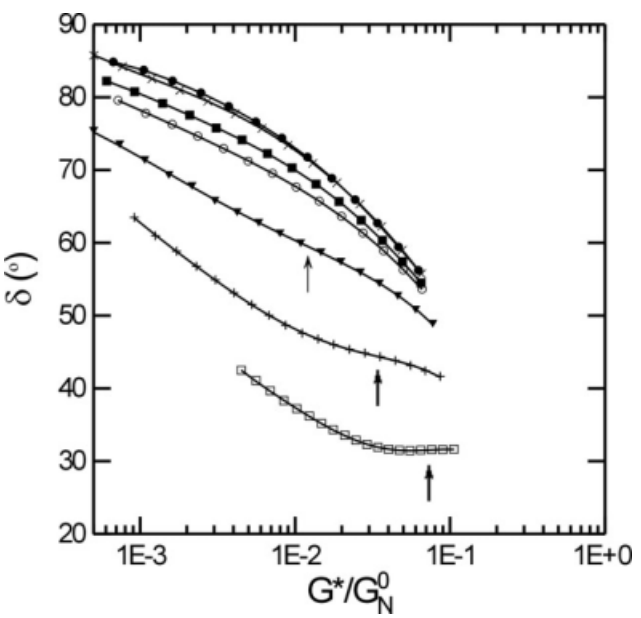

Figure 12 Van Gurp–Palmen plot corresponding to the original PE and modified HPE: (●) neat hydrogenated HDPE, (×) HPE-125, (■) HPE-250, (○) HPE-500, (▼) HPE-1000, (+) HPE-4000, and (□) HPE-5000. The continuous lines correspond to fitting polynomials employed to locate P_c, which is indicated by arrows, as explained in the text.

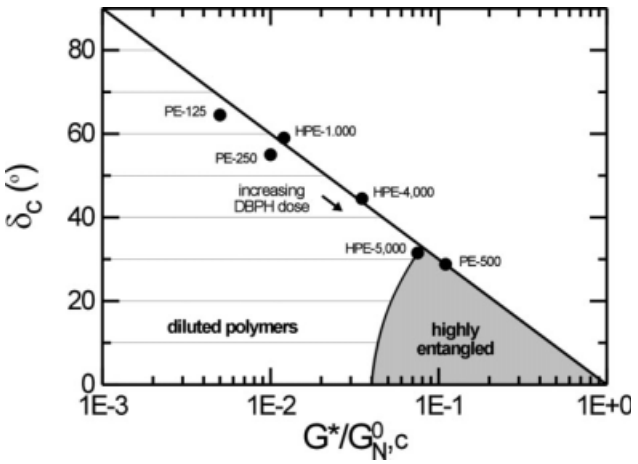

Figure 13 Evolution of the critical point (δ_c) of both PEs treated with increasing amounts of peroxide on the topology map. The arrow indicates the direction in which the peroxide dose increases.

CONCLUSIONS

By hydrogenating a commercial PE with terminal vinyl groups, we found it possible to compare the response of two PEs differing in the concentration of terminal vinyl groups, but identical otherwise, in the process of modification experiments when those polymers were crosslinked with different concentrations of an organic peroxide. Because the results obtained in this study show that the major structural difference between the hydrogenated and unhydrogenated samples was the terminal vinyl groups, we

concluded that the differences observed in the rate of the peroxide crosslinking reaction and rheological properties were attributable to the terminal vinyl groups.

A considerably larger amount of peroxide was required to induce equivalent molecular changes in the structure of HPE. η' and G' experienced significant changes in the terminal region with increasing concentration of peroxide. However, unhydrogenated samples with terminal vinyl groups crosslinked faster and possessed higher values of viscosity and elasticity compared to their corresponding hydrogenated samples. The hydrogenated samples demanded between 500 and 1000% excess in the amount of peroxide required for the unhydrogenated samples to produce equivalent levels of modification in the rheological properties of the modified polymers.

The position of the critical point on the Van Gurp–Palmen graphs of the modified polymers suggested that from a rheological point of view, they behaved in a similar manner to mixtures of linear and highly branched chains.

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