

Rheological study of linear high density polyethylenes modified with organic peroxide

Claudio J. Pérez, Guillermo A. Cassano, Enrique M. Vallés,
Marcelo D. Failla, Lidia M. Quinzani*

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

Received 7 September 2001; received in revised form 7 January 2002; accepted 9 January 2002

Abstract

Four high density polyethylenes were modified using different concentrations of an organic peroxide in order to change their molecular structure. The effects of the presence of vinyl groups in the original polymer molecules and of the peroxide concentration used in the modification process were analyzed. All the concentrations of peroxide used in this study were below the critical concentration that produces a macroscopic molecular network. The weight-average molecular weight of all the polyethylenes augments and the molecular weight distribution gets wider as the concentration of peroxide increases. These results support the general belief that the chain-linking reactions dominate the modification process. Evidence of the important role played by the vinyl groups is found not only in the change of the width of the chromatograms but also in the position of their maximums. The vinyl-containing polymers display the largest molecular changes for a given peroxide content. The magnitude of the viscous and elastic moduli of the polyethylenes goes up as the concentration of peroxide used increases showing the effect of the generated large molecules. The linear viscoelastic response of the modified polymers is thermorheologically complex. This complexity can be associated with the generation of branched molecules. For similar molecular weights and peroxide concentration, the flow activation energy displayed by the polyethylenes with larger concentration of vinyl groups is larger. This result suggest that a much more complex molecular structure is formed in the presence of vinyl groups. The dynamic moduli of the polymers were analyzed using the generalized viscoelastic model. The spectrum of relaxation times was determined for each polymer and analyzed as a function of the peroxide concentration. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Peroxide modification; Rheology

1. Introduction

The use of organic peroxides for the modification of molten polyethylene (PE) is a method frequently used in the industry to obtain polymers which have physical and mechanical properties different from the original materials [1–3]. The method is based on the formation of oxy-radicals due to the thermal decomposition of the peroxide. The oxy-radicals abstract hydrogen atoms from the macromolecules generating macro-radicals which mostly participate in combination reactions producing chain-linking, that is, cross-linking, long-chain branching, and chain extension [4–8]. The peroxide decomposition has to take place in the range of the processing temperatures of the polymer for the process to be considered useful. The modification of PE by reaction with organic peroxides is studied in many

publications in the literature. Many of them analyzed the use of large concentrations of peroxide in order to produce intensive chain-linking and to transform part of the material in an insoluble molecular network or gel ([5–7,9–19] among others). There are only a few publications that study the modification of PE using peroxide concentrations below the critical concentration to produce a gel [4,20–29]. At these relatively low peroxide concentrations, the modified PE is still thermoplastic. The molecular structure of the PE changes in such a way that the average molecular weights increase and the molecular weight distribution becomes wider, altering its properties in the molten and solid states.

There are many factors to be taken into account in the process of chain-linking when PE is exposed to peroxide attack in the melt. The main one is the molecular structure, which is given by the average molecular weights of the polymer, the distribution of molecular weights and the existence of tertiary carbons (branch points), and vinyl groups [4,7,10,16,19,23–26]. Other factors are the concentration

* Corresponding author. Tel.: +54-291-486-1700; fax: +54-291-486-1600.

E-mail address: poquinza@criba.edu.ar (L.M. Quinzani).

Table 1
Characteristics of the HDPE used in the present study

| Material | Origin | M_w (g mol ⁻¹) | PD | 1,2-Vinyl concentration (mol l ⁻¹) ^a |
|----------|--------------------------|---------------------------------|-----|---|
| PE1 | Du Pont de Nemours (USA) | 53 000 | 2.4 | 0.033 |
| PE2 | Petropol (Argentina) | 55 000 | 4.6 | 0.0047 |
| PE3 | Du Pont de Nemours (USA) | 83 000 | 2.3 | 0.035 |
| PE4 | Petropol (Argentina) | 79 000 | 3.9 | 0.0033 |

^a The concentration of vinyl groups is calculated using an extinction coefficient of 153 l mol⁻¹ cm⁻¹ [34].

and type of peroxide, temperature and additives [6,14,17,18,30]. The vinyl-containing polymers cross-link faster and produce higher final gel contents than saturated polyethylenes. Equivalent gel content can be obtained in the saturated materials when higher peroxide concentrations are used [7,10,19,23–26]. Also, the amount of peroxide needed to reach the gel point decreases as the molecular weight of the PE increases [10]. According to Hulse et al. [10], the molecular weight and molecular weight distribution of polyethylenes with low vinyl concentration have no effect on the cross-link efficiency calculated as the ratio between the theoretical expectation and the amount of peroxide needed to reach the gel point. The presence of chain branches in the PE molecules has been shown to affect the scission probability which seems to depend on the initial branch concentration [4,16].

Only a few papers may be found in the literature that deal with the rheological characterization of polyethylenes modified with organic peroxides below the gel point [4,20,22–27,29]. These works were performed using linear low-density polyethylenes (LLDPE) [23–26,29], high-density polyethylenes (HDPE) [4,20,22], and low-density polyethylenes (LDPE) [4,27]. As expected, the results presented in them indicate that an enhancement of all the viscous and elastic properties is produced when the amount of peroxide added increases. This effect is more noticeable at low shear and extensional deformation rates. In some cases it has been observed that at high shear rates, the viscous properties of the modified polymers tend to be lower than those of the original polyethylenes [4] and that there is an accentuation of the shear-thinning behavior with the peroxide concentration used [4,23–26]. A reduction in the die swell with increasing peroxide concentration [23–26] as well as a delay in the onset of melt fracture upon extrusion [29] have been observed. When the previously mentioned effects are analyzed as a function of the type of polyethylene used in the modification process, it is concluded that the enhancement of the rheological properties is more important in the HDPE and less important in the branched LLDPE and LDPE which are susceptible to higher degradation by scission reactions.

The main objective of the present paper is to study the effect of peroxide concentration on the molecular weights

and the rheological properties of a series of high-density polyethylenes with different original molecular weights and vinyl concentrations. The techniques of gel permeation chromatography, infrared spectroscopy, and dynamic rheometry are used to evaluate parameters that are used to characterize the molecular structure of the polymers. The morphological and mechanical properties of solid samples of modified polyethylenes will be presented in a second publication [31].

2. Experimental

2.1. Materials

Table 1 lists the polyethylenes used in this study and the calculated weight-average molecular weights (M_w) and polydispersities ($PD = M_w/M_n$). Fig. 1 shows the normalized chromatograms of the four original HDPE used in this study and are listed in Table 1. The chromatograms were obtained by gel permeation chromatography (GPC) using a Waters 150-C ALP/GPC equipped with a set of 10 μ m PLGel columns from Polymer Labs having nominal porous sizes of 10⁶, 10³, and 500 Å. The solvent used was 1,2,4-trichlorobenzene (TCB) at 140 °C. The molecular weights of the polymers were estimated following the standard calibration procedure using monodisperse polystyrene samples and the corresponding Mark–Houwink coefficients for polystyrene and linear polyethylene in TCB [32,33]. According to the chromatograms, PE2 and PE4 have a slightly broader molecular weight distribution than PE1 and PE3 and have tails of high and low molecular weight.

The concentration of vinyl groups of each polymer is presented in Table 1. This concentration was determined from infrared spectroscopic measurements (FTIR, Nicolet 520) performed on films. The vinyl concentration is calculated from the intensity of the 908 cm⁻¹ band using a molar extinction coefficient of 153 l mol⁻¹ cm⁻¹ [34]. The results

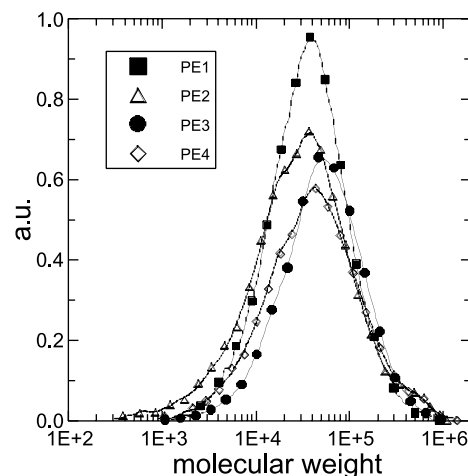


Fig. 1. GPC traces of the four original HDPE normalized to have the same area.

show that PE1 and PE3 have larger concentration of vinyl groups than the other two polymers. Approximately one vinyl group per molecule may be estimated for these two polymers taking into account the method of polymerization used in their synthesis.

2.2. Modification

The 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane was used as an initiator for the modification process. The resins were dissolved in xylene at boiling temperature and afterwards precipitated in cool methanol to obtain a fine powder. Fractions of these powders were then impregnated with different amounts of peroxide–hexane solution to give the desired final peroxide concentrations once the solvent was removed.

The impregnated polyethylenes were placed between 3 mm thick steel plates held apart by a 0.5 mm thick brass frame. The samples were then compression molded between the hot plates of an hydraulic press for 5 min at 170 °C and 10 bar. Then the pressure was relieved and the samples were kept at that temperature between the plates for an additional 15 min. The reaction time was chosen from the previously done rheological experiments, as the time needed to obtain constant values of the dynamic moduli. These moduli were continuously measured at 170 °C at a fixed frequency of 1 s⁻¹ using samples previously molded for 5 min at 170 °C and 10 bar. Bremner and Rudin [14] followed a similar procedure to study the kinetics of this type of modification reaction.

The modified polymers are designed as PE#-X, where # is the number that identifies the original PE and X corresponds to the concentration of peroxide used in the modification process in ppm. For example, the PE3-130 is the name of the polymer obtained by the modification of PE3 with 130 ppm of peroxide. No traces of gel were observed in any of the analyzed modified polymers after 6 h of Soxhlet extraction using boiling xylene.

2.3. Molecular characterization

GPC and FTIR were used to observe the change in molecular distribution and in the concentration of vinyl groups of the modified polymers, respectively. The chromatograms were obtained using the conditions previously cited for the characterization of the original polyethylenes. Consequently, the average molecular weights calculated for the modified polymers are underestimated since it is assumed that the polymer molecules are linear. Thus, the GPC characterization allows the performance of a qualitative comparison of the molecular weights as a function of peroxide concentration. The PE3 family of polymers were also characterized using the combined techniques of GPC and light scattering (MALLS).

2.4. Rheological characterization

The elastic or storage modulus, $G'(\omega)$, and the viscous or loss modulus, $G''(\omega)$, of all the materials were obtained in small-amplitude oscillatory shear flow experiments using a rotational rheometer from Rheometrics Inc. (model RDA-II). The tests were performed using parallel plates of 25 mm in diameter, a frequency range of 0.1–400 s⁻¹, and a temperature range of 140–200 °C. All the tests were performed using small strains to ensure the linearity of the dynamic responses [35]. Nitrogen atmosphere was used to prevent oxidation of the samples. The dynamic viscosity ($\eta'(\omega) = G''(\omega)/\omega$) and the phase angle ($\delta = \tan^{-1} G''/G'$), are parameters calculated from the dynamic moduli which are frequently used in this paper. All the runs were repeated using different polymeric samples. Several of the series of frequency sweeps at different temperatures were repeated twice with the same sample. Excellent agreement between the results was found in all the cases, indicating that no measurable degradation occurred during the rheological tests.

3. Results and discussion

3.1. Molecular characterization

Fig. 2 shows the normalized chromatograms of PE1 and PE2 and those of the corresponding modified polymers using different peroxide concentrations. Fig. 2(a), which corresponds to the PE1 family of polymers, shows a gradual enlargement in the width of the curves and a gradual shift in the maximum of the molecular weight distribution towards higher molecular weights with increase in the peroxide concentration. An increase in the width of the chromatograms of PE2 (Fig. 2(b)) is also observed although it is less noticeable. A slight shift in the maximum of the molecular weight distribution of these polymers is noticeable only when peroxide concentrations greater than 2000 ppm are used. The effect of peroxide on the shape of the chromatograms of the PE3 and PE4 family of polymers is equivalent to that observed in PE1 and PE2, respectively. The weight-average molecular weight and the polydispersity estimated from the chromatograms are listed in Table 2.

Fig. 3 shows the evolution of the concentration of vinyl groups in the four HDPE as a function of the peroxide concentration used in the modification. The amount of vinyl groups in PE1 and PE3 drops rapidly when the concentration of peroxide increases. The rate of consumption is similar in both the cases. PE1 reaches a very low value of vinyl content before traces of gel are observed in the sample (at ~2000 ppm). On the other hand, a measurable amount of vinyl groups still presented by the time evidences of gel formation are observed in PE3 (at ~500 ppm). The other two polyethylenes have a very low initial concentration of vinyl groups and hence, it is slightly

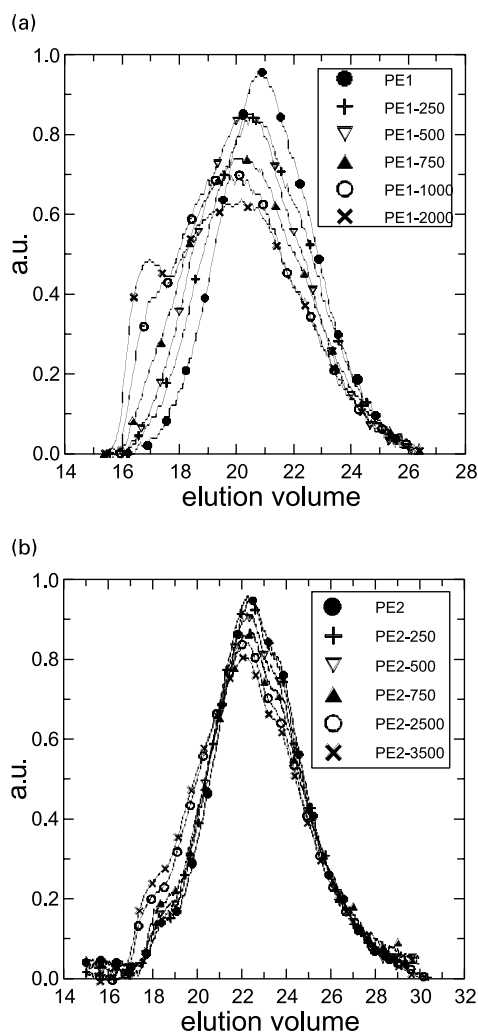


Fig. 2. GPC traces of PE1 (a) and PE2 (b), and the corresponding polymers obtained by reactive modification with different peroxide concentrations. Data curves have been normalized to have equal area.

affected by the modification process. In fact, they are about the minimum value detectable with the used procedure.

According to the GPC results, the chain-linking reaction is the one that prevails in the peroxide modification of all the

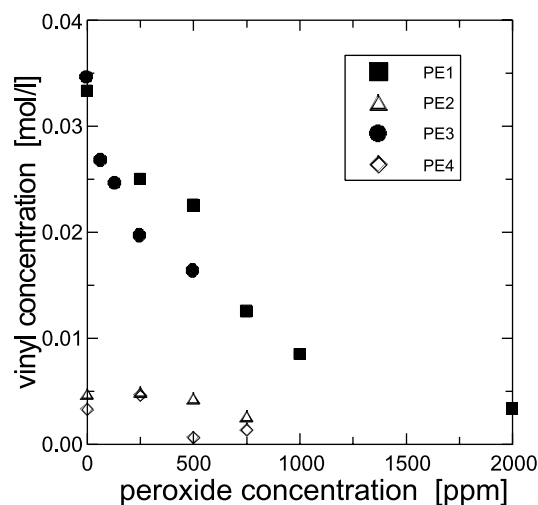


Fig. 3. Concentration of vinyl groups of the polyethylenes as a function of the peroxide concentration used in the modification process.

HDPE. For a given peroxide concentration, PE1 and PE3 show larger changes than PE2 and PE4 as shown by the data in Table 2. The larger initial concentration of vinyl groups present in PE1 and PE3 is the cause for the larger reactivity of these polymers. Several authors have previously suggested that the vinyl group participates actively in the modification process of PE [5,7,10,19]. A rapid decrease in the vinyl content is attributed to the fact that the allylic hydrogens present in the terminal vinyl groups are preferentially abstracted by the peroxide oxy-radicals. The generated macro-radicals then participate in chain-linking reactions.

The shift observed in the maximum of the chromatograms in Fig. 2(a) (which is also seen in the chromatograms of PE3) may be explained by the fact that in PE1 most of the initial molecules have terminal vinyl groups. Since these groups participate in the modification process and are consumed more rapidly, all the molecules, independent of their size, have a similar probability to participate in the chain-linking reactions and disappear to form larger molecules. On the other hand, when the concentration of

Table 2

Weight-average molecular weight and polydispersity (within brackets) calculated from GPC chromatograms assuming that the polymers are linear polyethylenes

| Peroxide concentration (ppm) | PE1 | PE2 | PE3 | PE4 |
|------------------------------|----------------------------|--------------|----------------------------|--------------|
| 0 | 53 000 (2.4) | 55 000 (4.6) | 83 000 (2.3) | 79 000 (3.9) |
| 65 | | | 98 000 (2.8) | |
| 130 | | | 108 000 (3.3) | |
| 250 | 71 000 (2.9) | 70 000 (4.2) | 117 000 (3.1) | 85 000 (4.7) |
| 500 | 78 000 (2.7) | 71 800 (4.6) | 155 000 (3.5) ^a | 94 000 (4.9) |
| 750 | 98 700 (3.8) | 76 000 (5.6) | | 95 000 (4.8) |
| 1000 | 130 000 (4.1) | | | |
| 2000 | 159 000 (5.2) ^a | | | |
| 2500 | | 87 000 (7.0) | | |
| 3500 | | 96 000 (7.7) | | |

^a The rheological characterization of these materials indicates the presence of micro-gels.

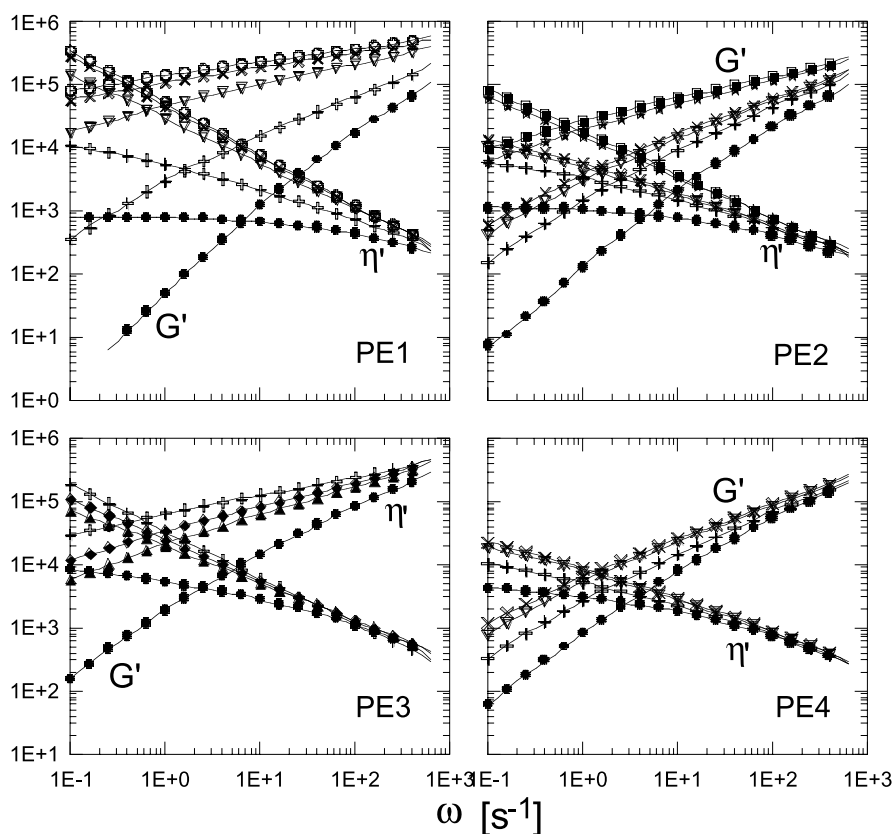


Fig. 4. Frequency dependence of the elastic modulus (G' , in Pa) and the dynamic viscosity (η' , in Pa-s) of all the family of polymers at 160 °C. Full lines: predictions of the multi-mode Maxwell model (Eq. (1)) with the corresponding coefficients shown later in Fig. 7. Symbols: (●): original polymers; (▲): 65 ppm; (◆): 130 ppm; (+): 250 ppm; (∇): 500 ppm; (×): 750 ppm; (○): 1000 ppm; (★): 2500 ppm; (■): 3500 ppm.

vinyl groups is small, the probability of a molecule to participate in a chain-linking reaction is mainly given by its size. Thus, the large molecules would have a higher chance to participate in the reactions than the small ones. This fact explains why the position of the maximum in the chromatograms of Fig. 2(b) is practically unaltered.

3.2. Rheological characterization

Fig. 4 shows the dynamic viscosity, $\eta'(\omega)$, and the elastic modulus $G'(\omega)$ of all the studied materials at 160 °C. The results of PE1-2000 and PE3-500 are not included in the figures because the rheological characterization of these polymers suggests the presence of micro-gels even though they were not detected during the solvent extraction with boiling xylene. In all the cases the modified materials show a progressive increase both in viscosity and in elasticity with increase in the amount of peroxide used, in agreement with the observations of other authors [4,20,22–27,29]. These effects are the result of the increasing amount of large macromolecules formed by the chain-linking reactions. Comparing PE1 and PE2, which have similar molecular weights, the effect is more noticeable in PE1, in agreement with the results of the molecular characterization. For example, the rheological behavior of PE1-250 is similar to

that of PE2-500. This means that in the case of PE2, which has a very low initial vinyl concentration, it is necessary to use a concentration of peroxide at least twice that in the case of PE1 to obtain similar modification results. Furthermore, the large increment in the rheological properties observed when PE1 was modified with 500 ppm was not obtained with PE2, not even when 3500 ppm was used. The same comment is valid for PE3 and PE4 although these two materials have slightly different original molecular weights. An equivalent result was obtained by Hulse et al. [10] and Smedberg et al. [7] who showed the important effect of the vinyl unsaturations on the chain-linking process. Hulse and coworkers found a 75% of cross-linking efficiency in a polyethylene with 0.5 vinyl groups/1000 C compared with approximately 30% obtained in the case of unsaturated polymers. Equivalently, Mandelkern [36] found that the irradiation dose to reach the gel point increases when the concentration of vinyl groups of a polyethylene decreases. This result was obtained by comparing irradiated samples of a HDPE (with approximately one vinyl group per molecule) with hydrogenated samples of the same polymer (with no vinyl groups).

The behavior of all the materials was also analyzed as a function of temperature in the range from 140 to 200 °C, using steps of approximately 10 °C. The curves of the linear

viscoelastic parameters of PE1, PE2, and PE4 show similar behavior with frequency and they may be shifted according to the time–temperature superposition principle [35] to build master curves of the dynamic material parameters. PE3 has no simple thermo-rheological behavior. Fig. 5 shows the master curves of the phase angle ($\delta(\omega)$) of the four HDPE. In the case of PE3, two pseudo-master curves are presented which are built by superposing the viscoelastic data at low and high frequencies, respectively. The fact that PE1, PE2, and PE4 are thermo-rheologically simple polymers means that all the relaxation processes that affect the rheological behavior in the covered range of frequencies have the same dependency with temperature. The shape of the $\delta(\omega)$ curves of PE3 and its thermo-rheologically complex behavior suggest the presence of some long-chain branches in this polymer. It has been proposed and experimentally confirmed [37,38] that long branches in polymers with a negative slope of the derivative of the radius of gyration with temperature ($\partial \ln \langle R^2 \rangle / \partial T$), like in the case of polymethylene chains, produce an increase in the values of the flow activation energy, when calculated from zero-shear-rate viscosity measurements.

With respect to the modified polymers, all of them present a thermo-rheologically complex behavior. The time–temperature superposition principle cannot be used with these polyethylenes in the whole range of frequencies covered. As an example, Fig. 6 shows the master curve of the phase angle of PE1 and the pseudo-master curves of the corresponding modified polymers that may be built by superposing the viscoelastic data at low frequencies. This procedure allows us to further analyze the temperature

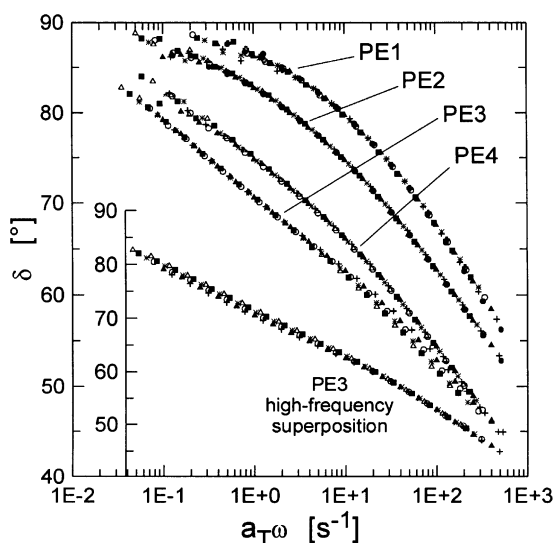


Fig. 5. Master curves of the phase angle of PE1, PE2, and PE4 and pseudo-master curve of PE3 obtained by the superposition of the data at small frequencies. Reference temperature: 160 °C. The additional data (plotted with respect to the small ordinate-axis) correspond to the pseudo-master curve of PE3 obtained by the superposition of the data at high frequencies. Different symbols correspond to different temperatures between 150 and 200 °C.

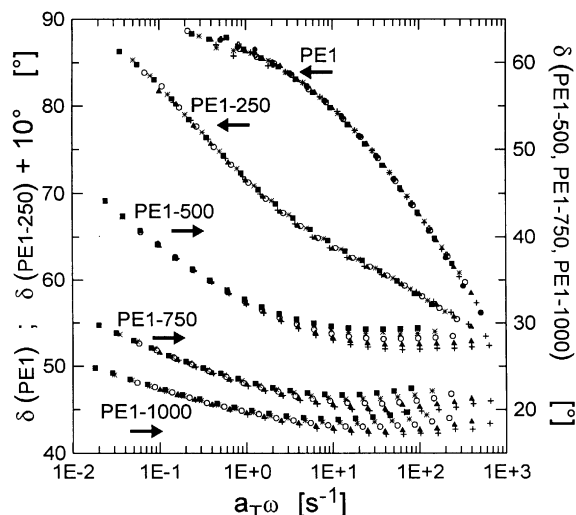


Fig. 6. Master curve of the phase angle of PE1 and pseudo-master curves of the modified PE1-*i* polymers obtained applying the time–temperature superposition principle in the range of small frequencies. Reference temperature: 160 °C. Different symbols correspond to different temperatures between 150 and 200 °C.

dependence of the low-frequency data, which are affected by the large relaxation processes. The thermo-rheological complexity of the modified polymers is a consequence of the long chain branches generated in the polymer molecules during the peroxide modification process.

The master curves and pseudo-master curves of the phase angles are constructed by shifting the data in the time scale by factors a_T . All the sets of a_T data calculated have an Arrhenius type of dependence with temperature, i.e. $\ln a_T \approx \Delta H/RT$, where ΔH is the flow-activation energy and R is the universal gas constant. Table 3 lists the values of ΔH for all the polymers.

The flow activation energies of PE1, PE2, and PE4 are in accordance with previously reported values for linear polyethylenes [39–41]. The flow activation energy reported in the case of PE3 and the modified polymers is the one which describes the temperature dependence of the slower relaxation processes, i.e. those that dominate the response of the polymers at small frequencies and that may be associated with the large-scale dynamics of the molecules. Only in the case of PE3, PE2-250, and PE4-250 it was also possible to shift the curves and superpose them in the range of large frequencies, as shown in Fig. 5 for PE3. The flow activation energies ($\Delta H'$) calculated in this way are listed within parenthesis in Table 3. These values are lower than those corresponding to the flow activation energies determined in the low frequency zone. These $\Delta H'$ describe the temperature dependency of relaxation processes that are several orders of magnitude faster than the larger ones previously mentioned. Studies performed on irradiated samples of PE1 and PE3 and on samples of hydrogenated polybutadienes modified with peroxide gave very similar values of $\Delta H'$ ($33.0 \pm 4.7 \text{ kJ mol}^{-1}$) [42].

The value of ΔH of the modified polymers, as well as that

Table 3

Flow activation energy obtained from the calculated temperature shift factors used to build master curves (original polyethylenes) and pseudo-master curves (modified polyethylenes) of the linear viscoelastic data. Bold numbers correspond to thermo-rheologically simple materials with unique ΔH . The rest are flow activation energies determined from low-frequency data. Numbers within brackets correspond to flow activation energies measured from high-frequency dynamic data

| Peroxide concentration (ppm) | ΔH (kJ mol ⁻¹) | | | |
|------------------------------|------------------------------------|-------------|----------------|-------------|
| | PE1 | PE2 | PE3 | PE4 |
| 0 | 25.9 | 28.8 | 45.3 (33.3) | 28.7 |
| 65 | – | – | 53.3 | – |
| 130 | – | – | 72.7 | – |
| 250 | 58.0 | 55.1 (39.5) | 107 | 51.1 (36.7) |
| 500 | 77.5 | 59.1 | – ^a | 47.8 |
| 750 | 85.6 | 56.0 | – | 59.4 |
| 1000 | 91.5 | – | – | – |
| 2000 | – ^a | – | – | – |
| 2500 | – | 67.7 | – | – |
| 3500 | – | 76.3 | – | – |

^a The rheological characterization of these materials indicates the presence of micro-gels.

of PE3, corresponds to molecular structures more complex than that of the linear polymers. It is interesting to observe that the modified polymers of the PE2 and PE4 family obtained with 250, 500, and 750 ppm have similar flow activation energies (average $\Delta H = 54.8 \pm 4.6$ kJ mol⁻¹) which are also similar to the ΔH of PE1 and PE3 modified with the smaller concentrations of peroxide (PE1-250 and PE3-65). These results suggest that, from the point of view of the thermal response, the branched molecular structure obtained in all these cases are equivalent. Furthermore, since these values of ΔH are also similar to the flow activation energy of LDPE (55.3 kJ mol⁻¹) [41], it may be concluded that the molecular structure of these polymers may be similar to the conventional branched structure of polyethylenes. In the case of PE1 and PE3, the value of ΔH keeps increasing as the peroxide concentration used increases. The same trend is observed in the case of PE2 modified with concentrations greater than 2000 ppm. These values of ΔH suggest a much more complex molecular structure that may be of the type of branches-on-branches. The analysis of the flow activation energies of all the polymers agrees with the fact that the vinyl groups have an important effect on the peroxide modification process generating more complex molecular structures.

It may be interesting to compare the results obtained from the peroxide modification process of HDPE with those of a linear conventional polyethylene modified by irradiation with different doses. When PE1 is modified by irradiation at room temperature it is observed that the GPC chromatograms change with the irradiation dose following a similar pattern to those of the polyethylenes with no vinyl groups. The concentration of vinyl groups is observed to decrease with the increase in the irradiation doses used although a large concentration of vinyl groups is still present by the time the gel point is reached at approximately 30 kGy [42]. All the irradiation modified materials are also thermo-rheologically complex polymers. The flow activation

energy of these materials increases with the irradiation dose and the largest value calculated is 63 kJ mol⁻¹ at 20 kGy. This value is similar to the flow activation energy of the modified polymers of the PE2 and PE4 family and to the flow activation energy of PE1-250 and PE3-65. Again, it may be concluded that when the modification process is controlled by the molecular weight of the molecules rather than by the number of molecules of each weight, the modification process proceeds in such a way that the generated branched molecular structures are equivalent, at least from the rheological point of view.

3.3. Modeling of the linear viscoelastic results

The viscoelastic response of the polymer exposed to flows of small deformations is successfully described by the general linear viscoelastic model which is well described in several standard references [35,43]. For the particular choice of a relaxation modulus described by the sum of terms, which exponentially decay with time (multi-mode Maxwell model), the dynamic material parameters are described by the following relations

$$G'(\omega) = \sum_{k=1}^N \frac{\eta_k \lambda_k \omega^2}{1 + \lambda_k^2 \omega^2} \quad (1)$$

$$G''(\omega) = \omega \eta'(\omega) = \sum_{k=1}^N \frac{\eta_k \omega}{1 + \lambda_k^2 \omega^2}$$

where the set of constants λ_k and η_k constitute the spectrum of relaxation times and viscosities. The spectrum is reduced to a discrete number of elements by organizing the relaxation times in decreasing order and setting λ_k and η_k to zero for k greater than some finite number N . The relaxation modulus is then dominated by the largest relaxation time, λ_1 .

The rheological behavior of the polymers in the range of

frequencies covered in the present work is affected by the intermediate and long time scale molecular dynamics, i.e. entanglement and flow behavior. The long branches in the polymer molecules strongly suppress the translational motions of the whole molecules which, however, can still change their configurations by retracting the long branches along their primitive path, pushing out unentangled loops into the surrounded matrix [37]. This additional relaxation mechanism causes a large increase in the characteristic zero-shear-rate relaxation time, λ_0 , of long branched polymers with respect to the corresponding value for linear molecules of similar (high) molecular weight. At low frequency, the rheological response of the polymers is dominated by the slower relaxation processes, allowing the analysis of changes in the large-scale molecular structure. The relaxation processes at higher frequencies are dominated by shorter-range interactions which may be associated with molecular movements of a smaller scale than the previous ones but larger than the distance between entanglements that mainly affect the plateau region. In the case of the family of polyethylenes analyzed in this paper, the relaxation processes at this range of frequencies should be very similar in all the polymers because they should all have a similar intermediate scale molecular structure.

The terminal relaxation spectra of each material is calculated by minimizing the sum of the set of functions:

$$F_j = [\log G'_j - \log G'(\omega_j)]^2 + [\log G''_j - \log G''(\omega_j)]^2 \quad (2)$$

for $j = 1, \dots, m$ where m is the number of experimental data. Each term in Eq. (2) represents the difference between the measured dynamic modulus (elastic or viscous) and the corresponding one calculated with Eq. (1) at the same frequency. The minimization is done using the nonlinear regression method of Levenberg–Marquard [44].

Fig. 7 shows the set of constants λ_k and η_k of all the polymers determined using the above mentioned minimization procedure and the dynamic moduli of all the polymers at 160 °C. The solid lines in Fig. 4 correspond to the predictions of Eq. (1) using the calculated relaxation spectra at 160 °C. As can be observed, the fitting obtained using five modes of relaxation is very good in all the cases. Fig. 7 clearly shows that the peroxide modification process produces a modification of the molecular structure of all the HDPE that is mainly reflected in the longer relaxation processes, i.e. large-scale molecular structure. The range of relaxation times determined for each sample is practically the same for all the cases since we are limited by the range of frequencies used to calculate the dynamic data. The value of η_k associated with each relaxation time gives the importance of that relaxation mode. As can be seen in Fig. 7, in all the cases there is a large increment in the importance of the longer relaxation processes while the lower ones remain practically unaltered. These results reflect the different rheological behavior of materials, which although having similar microstructure, differ in their average large-scale molecular structure. As expected, the effect is more noticeable in PE1

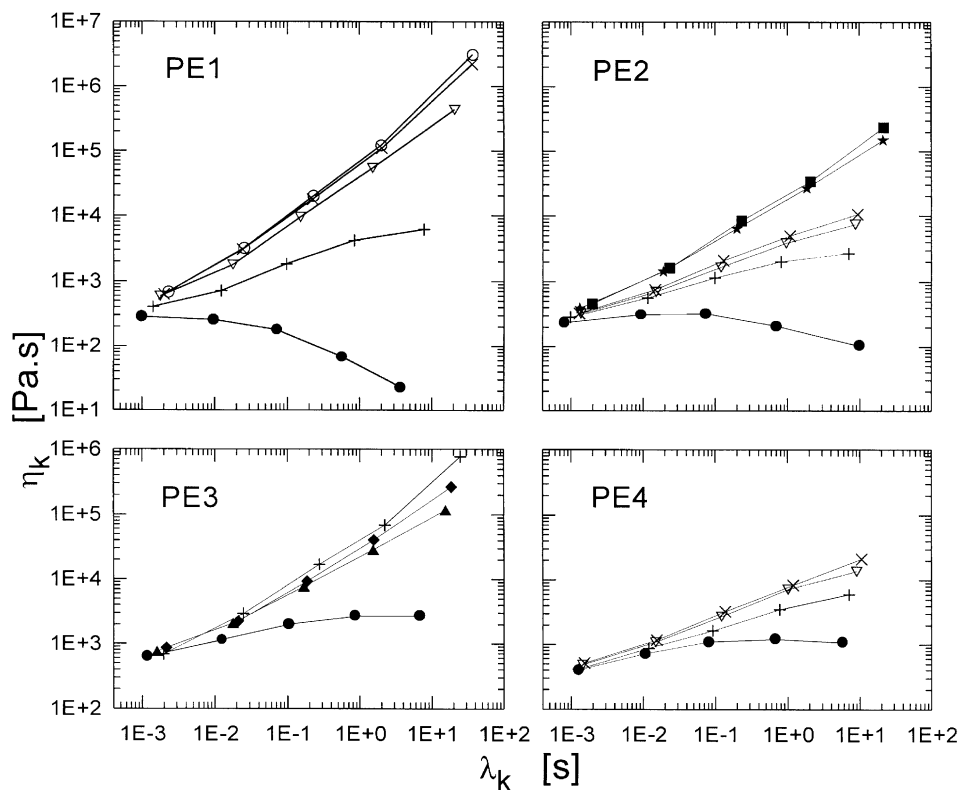


Fig. 7. Spectrum of relaxation times $\{\lambda_k, \eta_k\}$ obtained from the fitting of the dynamic data at 160 °C shown in Fig. 4 to the multi-mode Maxwell model. Symbols: (●): original polymers; (▲): 65 ppm; (◆): 130 ppm; (+): 250 ppm; (▽): 500 ppm; (×): 750 ppm; (○): 1000 ppm; (★): 2500 ppm; (■): 3500 ppm.

Table 4

Zero-shear-rate viscosities and relaxation times predicted by the multi-mode Maxwell model using the coefficients shown in Fig. 7

| Peroxide (pm) | $\eta_0 = \sum_k \eta_k (\text{Pa s}) - \lambda_0 = \sum_k \eta_k \lambda_k / \sum_k \eta_k (\text{s})$ | | | |
|---------------|---|--------------|--------------|-------------|
| | PE1 | PE2 | PE3 | PE4 |
| 0 | 808– 0.71 | 1190– 1.02 | 9160– 2.27 | 4490–1.58 |
| 65 | | | 156 400–11.8 | |
| 130 | | | 319 500–15.7 | |
| 250 | 13 300– 3.86 | 6770– 3.06 | 862 500–22.3 | 12 400–3.62 |
| 500 | 501 000–18.2 | 14 100– 4.89 | | 25 100–5.4 |
| 750 | 2 340 000–34.5 | 18 800– 5.58 | | 34 400–6.8 |
| 1000 | 3 280 000–35.4 | | | |
| 2500 | | 184 000–17.4 | | |
| 3500 | | 282 000–18.3 | | |

and PE3 than in the other two polymers. The largest relaxation time determined in the case of PE1 and PE3 family of polymers increases by a factor of 10 and 4, respectively, and strongly dominates the rheological response at low frequencies of all the modified polymers. As expected, the spectrum of relaxation times and viscosities determined for the PE2-500 and PE2-750 polymers are very similar to that of PE1-250.

In the limit of small frequencies, the dynamic viscosity approaches the zero-shear-rate viscosity, η_0 . Among the polymers studied in this paper, η_0 can be determined with precision only in the case of the linear polymers (see Fig. 4). Nevertheless, the spectrum of relaxation times permits the calculation of a zero-shear-rate viscosity and a zero-shear-rate relaxation time as:

$$\eta_0 = \sum_k \eta_k \quad \lambda_0 = \sum_k \eta_k \lambda_k / \sum_k \eta_k \quad (3)$$

The zero-coefficients predicted in this way will be under-

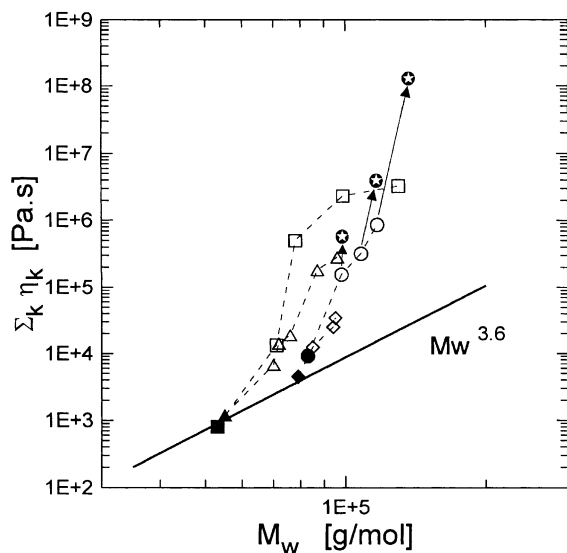


Fig. 8. Weight-average molecular weight dependency of the zero-shear-rate viscosity of all the polymers at 160 °C. Symbols: (■): PE1; (□): PE1-i; (▲): PE2; (△): PE2-i; (●): PE3; (○): PE3-i; (⊕): PE3-i with η_0 calculated using Carreau–Yasuda model and M_w calculated with GPC-MALLS; (◆): PE4; (◇): PE4-i. Full line: $\eta_0 \sim M_w^{3.6}$.

estimated. The underestimation will become more intense as the peroxide concentration increases because the measured dynamic data of the branched polymers get more shear-thinning and farther away from the zero-shear region as the molecular structure gets more complex.

Table 4 shows the predicted η_0 and λ_0 . The zero-shear-rate viscosities are plotted in Fig. 8 as a function of the weight-average molecular weight of the polymers. A line of slope 3.6 has been added to compare the results with the theoretical $M_w^{3.6}$ dependency expected for η_0 in the case of materials with linear molecules [39,43]. The data plotted in Fig. 8 show the effect of both the molecular weight and the chain branching of the molecules. Even though both the weight-average molecular weight and the zero-shear-rate viscosity of the modified polymers are underpredicted, the results of Fig. 8 agree with the behavior expected for branched polymers. Results from GPC-light scattering for PE3-65, PE3-130, and PE3-250 show that the weight-average molecular weights are 0.6, 8.1, and 17% larger, respectively, than the ones estimated from GPC alone. On the other hand, the differences between the true zero-shear-rate viscosities and those calculated with the Maxwell model are expected to be much greater than 17%. For example, the Carreau–Yasuda model [43], which is known to give close fittings of viscosity data for several kinds of polymer melts, predicts zero-shear-rate viscosities for PE3-65, PE3-130, and PE3-250 that are 3.7, 12.4, and 150 times larger than those reported in Table 4. This means that the results will fall very far from the lines of slope 3.6 even if they are shifted to the correct molecular weight (see Fig. 8).

4. Conclusions

The use of low concentrations of an organic peroxide in the modification of linear polyethylenes produces changes in their molecular structures. According to the GPC results, the chain-linking reaction is the one that prevails. The average molecular weights of all the polyethylenes increase as the concentration of peroxide increases although the

polyethylenes with vinyl groups display the largest increase for a given peroxide concentration and original molecular weight. The change in the width and the position of the maximum in the chromatograms with the amount of peroxide used in the modification shows that the presence of vinyl groups plays an important role in the process.

The rheological behavior of all the modified polymers is characteristic of materials with complex molecular structure. The polymers have thermo-rheologically complex behavior with flow activation energies that increase with increase in the peroxide content. Low concentrations of peroxide generate materials with flow activation energies similar to that of low-density polyethylenes. The peroxide modification process produce changes in the molecular structure of linear polyethylene that is mainly reflected in the slow relaxation processes, i.e. the large-scale molecular structure. For a given initial molecular weight and concentration of peroxide, all the analyzed rheological parameters of the modified polyethylenes with relatively large content of initial vinyl groups are much larger than those of materials with practically no vinyl groups in their original structure. This effect is manifested mainly at low frequencies.

Acknowledgements

This work was supported by the National Research Council of Argentina (CONICET), the Agencia Nacional de Promoción Científica y Tecnológica and the Universidad Nacional del Sur.

References

- [1] Lambla M. *Macromol Symp* 1994;82:37–45.
- [2] Xantos M. *Reactive extrusion*. New York: Hanser, 1992.
- [3] Krentsel BA, Kissin YV, Kleiner VI, Stotskaya LL. *Polymers and copolymers of higher α -olefins*. Chemistry, technology, applications. Munich: Hanser, 1997. p. 299.
- [4] Lem KW, Han CD. *J Appl Polym Sci* 1982;27:1367–83.
- [5] Bremner T, Rudin A, Haridoss S. *Polym Engng Sci* 1992;32:939–43.
- [6] Gloor PE, Tang Y, Kostanska AE, Hamielec AE. *Polymer* 1994;35:1012–30.
- [7] Smedberg A, Hjertberg T, Gustafsson B. *Polymer* 1997;38:4127–38.
- [8] Pedernera M, Sarmoria C, Vallés EM, Brandolin A. *Polym Engng Sci* 1999;39:2085–95.
- [9] Narkis M, Miltz J. *J Appl Polym Sci* 1969;13:713–20.
- [10] Hulse GE, Kersting RJ, Warfel DR. *J Polym Sci, Polym Chem* 1981;19:655–67.
- [11] Boer J, Pennings AJ. *Polymer* 1982;23:1944–52.
- [12] Narkis M, Raiter I, Shkolnik S, Sigmann A. *J Macromol Sci, Phys* 1987;B26:37–58.
- [13] Lambert WS, Phillips PJ. *Polymer* 1990;31:2077–82.
- [14] Bremner T, Rudin A. *J Appl Polym Sci* 1993;49:785–98.
- [15] Lambert WS, Phillips PJ, Lin JS. *Polymer* 1994;35:1809–18.
- [16] Sajkiewicz P, Phillips PJ. *J Polym Sci, Polym Chem* 1995;33:949–55.
- [17] Bremner T, Rudin A. *J Appl Polym Sci* 1995;57:271–86.
- [18] Kang TK, Ha CS. *Polym Testing* 2000;19:773–83.
- [19] Palmlof M, Hjertberg T. *Polymer* 2000;41:6497–505.
- [20] Kim KJ, Kim BK. *J Appl Polym Sci* 1993;48:981–6.
- [21] Suwanda D, Balke ST. *Polym Engng Sci* 1993;33:455–65.
- [22] Harlin A, Heino EL. *J Polym Sci, Polym Phys* 1995;33:479–86.
- [23] Lachtermacher MG, Rudin E. *J Appl Polym Sci* 1995;58:2077–94.
- [24] Lachtermacher MG, Rudin E. *J Appl Polym Sci* 1995;58:2433–40.
- [25] Lachtermacher MG, Rudin E. *J Appl Polym Sci* 1996;59:1213–21.
- [26] Lachtermacher MG, Rudin E. *J Appl Polym Sci* 1996;59:1755–85.
- [27] Ghosh P, Dev D, Chakrabari A. *Polymer* 1997;38:6175–80.
- [28] Abraham D, George GE, Francis DJ. *Polymer* 1998;39:117–21.
- [29] Kim YC, Yang KS. *Polym J* 1999;31:579–84.
- [30] Chodák I, Romanov A, Rätzsch M, Haudel G. *Acta Polym* 1987;38:672–4.
- [31] Pérez CJ, Cassano GA, Vallés EM, Quinzani LM, Failla MD. To be published.
- [32] Barlow A, Wild L, Ranganath R. *J Appl Polym Sci* 1977;21:3319–29.
- [33] Wild L, Ranganath R, Knoblock K. *Polym Engng Sci* 1976;16:811–6.
- [34] Dole M. In: Dole M, editor. *The radiation chemistry of macromolecules*, vol. 1. New York: Academic Press, 1972. p. 282, chapter 12.
- [35] Ferry JD. *Viscoelastic properties of polymers*. 3rd ed. New York: Wiley, 1980.
- [36] Mandelkern L. In: Dole M, editor. *The radiation chemistry of macromolecules*, vol. 1. New York: Academic Press, 1972. p. 316, chapter 13.
- [37] Graessley WW. *Macromolecules* 1982;15:1164–7.
- [38] Carella JM, Gotro JT, Graessley WW. *Macromolecules* 1986;19:659–67.
- [39] Raju VR, Smith GG, Marin G, Knox JR, Graessley WW. *J Polym Sci, Part B: Polym Phys Ed* 1979;17:1183–95.
- [40] Quinzani LM, Vallés EM. *Rev Latinoamer Ing Quím y Quím Aplic* 1987;17:121–34.
- [41] Wasserman SH, Graessley WW. *Polym Engng Sci* 1996;36:852–61.
- [42] Pérez CJ, Vallés EM, Quinzani LM, Failla MD. *Proceedings of the Third Mercosur Congress on Process Systems Engineering and 1st Mercosur Congress on Chemical Engineering*. Universidad Nacional del Litoral, Santa Fe, Argentina, November, 2001, vol. II, p. 763–8.
- [43] Bird RB, Armstrong RC, Hassager O. *Dynamics of polymeric liquids*. 2nd ed. New York: Wiley, 1987.
- [44] Press WH, Flannery BP, Teukolsky SA, Vetterling WT. *Numerical recipes*. Cambridge: Cambridge University Press, 1986.