

Entanglement Network and Relaxation Temperature Dependence of Single-Site Catalyzed Ethylene/1-Hexene Copolymers

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ABSTRACT: In this work, we investigate the linear viscoelastic response of high molecular weight ethylene/1-hexene copolymers, characterized by a narrow molecular weight distribution and comonomer content in the range from 0 to 10 mol %. A variation in the entanglement plateau modulus has been found in agreement with the recently developed packing length model. The packing model applied to viscoelastic data suggests decreased values of the characteristic ratio, accordingly with recent computer simulation results. The flow activation energy increases as the side chain content increases. This feature is thought to be related to the mobility of the molecules. The presence of side branches due to the comonomer hin-

ders the mobility of the molecules, and increases the thermal barrier for the segmental motion. Then in the comonomer content range studied, the increase of the flow activation energy goes parallel with a decrease in the characteristic ratio. This result suggests that more parameters than only the stiffness of the chain modulate the thermal dependence of viscoelastic properties. A more refined study is necessary combining experiments with computer simulations in order to elucidate these aspects. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1564–1569, 2008

Key words: copolymerization; polyolefins; viscoelastic properties

INTRODUCTION

The study of the relationship between the macromolecular chemical structure and physical properties and entanglement features has paid significant interest along the last decade, especially in the case of polyolefins obtained from single-site catalysts (SSC).^{1–7} These polymers are considered as physical models, mostly because of their homogeneous molecular architecture. Recent studies have suggested a strong effect of side chains in the macromolecular conformation affecting to macroscopic features.^{5–7} In particular, it is possible to relate the size of polymer coils to the extent to which they interpenetrate each other, and then to the entanglement state. An example of this is the so-called packing length model, which has been proved to predict the entanglement ability of flexible chains as a function of their dimensions. Furthermore, the model, applied to polyolefins, connects the entanglement state with the chemical structure

assuming that the chain trans/gauche ratio configuration is the same for all polyolefins.⁸ In this work, we investigate the rheological behavior of high molecular weight ethylene/1-hexene copolymers with narrow molecular weight distribution with a comonomer content in the range from 0 to 10 mol %. To our knowledge, the entanglement features of ethylene/1-hexene copolymers have not been previously explored in this range of comonomer content, although some studies can be found for ethylene/propylene, ethylene/1-butene, ethylene/1-octene, and ethylene/styrene copolymers.^{3–7}

EXPERIMENTAL

Polyethylene rich random copolymers with 1-hexene were synthesized using a single-site catalyst system. Commercial $[\text{Me}_2\text{Si}(\text{Cp}^*)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (from Boulder Sc. Co., USA) and the cocatalyst methylaluminoxane (MAO) purchased from Witco GmbH (Bergkamen, Germany, 10 wt % MAO in toluene) were used without further purification. HPLC grade toluene (from Scharlau Chimie, Barcelona) was used as polymerization medium. Ethylene and nitrogen (purchased from Air Liquide, Madrid) as well as toluene were further purified by passing through a series of columns containing molecular sieves and

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TABLE I
Physical Properties of the Copolymers Studied

Sample	E/H M/M ^a	Branching CH ₃ /1000 C	M_w (kg/mol)	M_w/M_n	T_m (°C)	α	G_N^0 (MPa) ^b	G_N^0 (MPa) ^c	G_N^0 (MPa) ^d	M_e (kg/mol) ^e	C_∞	E_d (kJ/mol)
pEH0 ^f	0	0	500–2300 ^f	2.0–2.5 ^f	134.2	0.70	—	—	1.6–2.0 ^f	1.30–1.20 ^f	7.11	22.9
bEH10	0.10	10.5	215	2.3	116.3	0.48	1.57	1.60	1.57	1.46	7.02	31.2
bEH15	0.35	15.0	200	2.1	106.5	0.34	1.33	1.33	1.32	1.75	6.84	32.5
bEH23	0.42	23.3	350	2.0	97.7	0.25	1.13	1.18	1.19	1.97	6.76	34.5
bEH30	0.50	30.0	n.m.	n.m.	91.2	0.18	1.11	1.09	1.10	2.14	6.77	36.5
bEH35	0.70	35.7	370	2.0	75.4	0.16	0.99	1.04	1.03	2.24	6.75	37.3
bEH42	1.00	42.0	340	2.1	66.8	0.09	0.93	0.97	0.95	2.40	6.71	38.6

^a Ethylene/1-hexene molar ratio in reactor feed.

^b From eq. (2).

^c From eq. (3).

^d From eqs. (4)–(6).

^e From eq. (1) with $K = 4/5$ and G_N^0 values obtained from method (c): see text.

^f Results obtained in our laboratory for linear samples [3,4].

Al₂O₃, to remove residual traces of moisture and oxygen. All materials were handled and stored under dry nitrogen atmosphere. Copolymerizations were carried out in a glass autoclave (Büchi). The reactor (1 L of volume) was filled with toluene (400 mL), 1-hexene (variable ethylene/1-hexene reactor feed molar ratio), and part of the needed amount of MAO under nitrogen atmosphere. Toluene was purchased from Scharlau Chemie and 1-hexene from Sigma-Aldrich (Dorset, United Kingdom). After thermostating the reactor at the polymerization temperature, nitrogen was removed *in vacuo* and the reaction mixture saturated with ethylene. Then the rest of the MAO was added and the reactor pressurized with ethylene at the polymerization reaction. Finally, the catalyst in toluene solution was injected into the reactor. During the polymerization the ethylene pressure was kept constant and the ethylene consumption measured by a mass flow controller (Brooks Instrument B.V., Veenendaal, Netherlands). The polymerization conditions used were [cat] = 20 μ mol/L, Al : Ti = 2000, ethylene pressure = 3 bar, polymerization temperature = 35°C, and polymerization time = 1.5 h. The copolymerization reaction was stopped by degassing the reactor to the atmosphere and adding a solution of 20 mL 5% HCl in methanol. Finally, the reaction products were converted into small pieces, washed with acidic (containing 5% HCl) methanol (200 mL), toluene (200 mL), and with acetone (200 mL), and filtered. Lastly, the polymers were transfer to a rotary evaporator and dried at 60°C to constant weight. All the chemicals were purchased from Scharlau Chemie.

SEC traces have been obtained in a 150CV Waters GPC coupled with refractive index and viscosity detectors. The solvent used for the analysis was 1,2,4-trichlorobenzene (TCB), the flow rate was 1.0 mL/min and the temperature was 145°C. The SEC-viscosity system was calibrated using polystyrene standards. All samples are characterized by a nar-

row molecular weight distribution ($M_w/M_n \sim 2$) and a similar weight average molecular weight (see Table I).

The samples were also analyzed by ¹³C-NMR spectroscopy to obtain the comonomer content (see Table I). The samples were dissolved in hot TCB and d⁶-benzene. Spectra were recorded at 100°C on a Bruker DRX 500 spectrometer operating at 75 MHz. The pulse repetition rate was 1.5 s; the pulse angle 90°, and at least 2000 pulse sequences were recorded. Carbon signals and comonomer contents were assigned and calculated according to the literature.⁹

Melting temperatures (T_m) and crystallinities (α) were determined in a Perkin-Elmer DSC7 differential scanning calorimeter (a value of 288.4 J/g was used as the reference melting enthalpy for 100% crystalline polyethylene). Indium was used for the calibration of the temperature scale. Melting features were measured upon the second heating of the samples from 25 to 160°C at a heating rate of 10°C/min. A previous study about the structural aspects of this type of polymers, including melting behavior and microstructure obtained from wide angle X-ray scattering and Raman spectroscopy can be found elsewhere.¹⁰ Anyway, the general trends for T_m and α observed Table I reflect the progressive and similar decrease in the concentration and length of crystallizable ethylene sequences in the copolymers as the comonomer content increases. This behavior is the expected for polymeric systems where comonomer is excluded from the crystal.

The stabilized polymers were compression molded at 150°C, using a pressure of 50 bar for 5 min, and subsequently quenched to room temperature. The films thickness was adjusted to 1 mm, a suitable one to meet the requirements of the rheological technique. Small-amplitude oscillatory viscoelastic measurements were carried out in a Bohlin CVO stress-

controlled rheometer using the parallel disk (15 and 25 mm diameter) geometry, covering an angular frequency range between 6.28×10^{-3} and 6.28×10^2 rad/s, well inside the linear viscoelastic region. The following viscoelastic functions were measured as a function of the angular frequency, ω , at different temperatures: storage modulus, G' ; loss modulus, G'' . The temperature range of measurements was from melting temperature to 190°C . One of the most interesting viscoelastic functions exhibited by polymeric systems is the modulus associated with the entanglement plateau, G_N^0 . According to the rubber elasticity theory, G_N^0 is defined by:

$$G_N^0 = \frac{K\rho RT}{M_e} \quad (1)$$

where M_e is the molecular weight between entanglements; ρ , the melt density; R , the gas constant; T , the absolute temperature; and K , a constant that equals to 1 or $4/5$ depending upon convention.^{11,12} Notwithstanding, the actual value of K is currently being a question of debate.^{13,14} There is a number of semi-empirical methods to obtain G_N^0 from the relaxation spectrum.¹⁵ Among all these methods, we have selected **(a)** the Marvin-Oser correlation based on the maximum exhibited by G'' :

$$G_N^0/G''_{\max} = 4.83 \quad (2)$$

and **(b)** the Wu method based on the cross-point modulus (G_x) coordinate between G' and G'' functions and polydispersity index¹⁷:

$$\log(G_N^0/G_x) = 0.38 + [2.63 \log(M_w/M_n)] / [1 + 2.45 \log(M_w/M_n)] \quad (3)$$

However, the preferred method to estimate G_N^0 is **(c)** the integration of either the relaxation time spectrum, $H(\tau)$, or the loss modulus peak dispersion, $G''(\ln \omega)$. This method is based on the fluctuation-dissipation theorem applied to the relaxation flow transition,¹⁸ which gives rise to:

$$G_N^0 = G_{\text{FT}}(0) - G_\infty = \frac{2}{\pi} \int_{-\infty}^{+\infty} [G''(\omega) - G''_{\text{MT}}(\omega)] d \ln \omega \quad (4)$$

$G_{\text{FT}}(0)$ is the highest value of the modulus in the terminal region, G_∞ , the equilibrium modulus (usually set as 0), and $G''_{\text{MT}}(\omega)$ denotes the contribution of the Rouse modes and the main transition to G'' at high frequencies. However, in the materials studied here, the main transition comes about at frequencies experimentally inaccessible. Then, the integration is

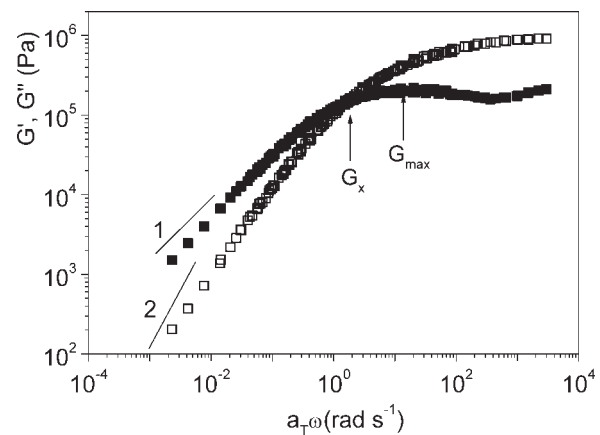


Figure 1 Linear viscoelastic spectrum of the copolymer bEH42 at 190°C : (\square) G' and (\blacksquare) G'' . The typical dependencies $G'' \propto \omega$ and $G' \propto \omega^2$ of the terminal region, and the characteristic values of G_x and G''_{\max} are indicated.

only possible by extrapolating G'' . A simple straight line from the peak in G'' to higher frequencies is generally adopted as a rule of thumb.¹⁵ However, the experiments performed on monodisperse samples show a power law, $G'' \propto \omega^{-0.25}$, in the frequency range $\omega > \omega_{\max}$, also predicated by the recent Linkhtman-McLeish reptation approach.¹⁹ Therefore, to account for the characteristic asymmetry, we have applied an exponentially modified Gaussian function to our results:

$$f(x) = \frac{A}{\beta} \exp\left[\frac{1}{2} \left(\frac{\omega}{\beta}\right)^2 \frac{x - c_{\max}}{\beta}\right] \int_{-\infty}^z \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{y^2}{2}\right) dy \quad (5)$$

$$z = \frac{x - c_{\max}}{\omega} - \frac{\omega}{\beta} \quad (6)$$

$f(x)$ is $G''(\ln \omega)$; A is the area under the curve [then $G_N^0 = 2A/\pi$ from eqs. (3) and (4)]; w/β is a parameter that accounts for the asymmetry; and c_{\max} the center coordinate. We have fixed the parameter $w/\beta \sim 0.6$, so that for all the samples this value gives to the same $\omega^{-0.25}$ dependency in the high frequency zone.

DISCUSSION AND CONCLUSIONS

The time-temperature superposition principle was found to be applicable for all materials within the temperature range tested. From now all the results shown are referred to a temperature of 190°C . Figure 1 shows the viscoelastic spectrum master curve of one of the copolymers studied. The system shows the expected behavior at very low frequencies ($G' \propto \omega^2$ and $G'' \propto \omega$), envisaged from the microscopic viewpoint by the reptation model.¹² In this figure we

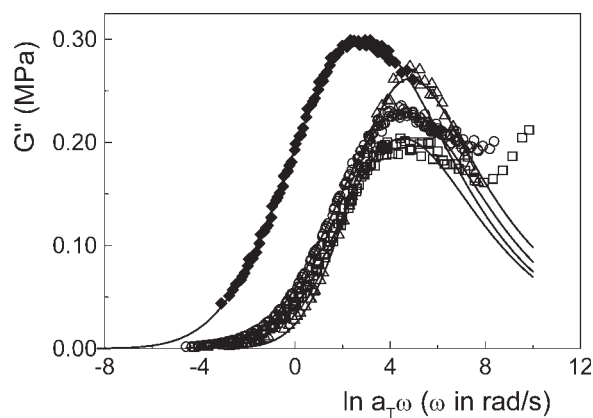


Figure 2 Loss modulus peak dispersion as a function of the natural logarithm of the angular frequency for some of the copolymers studied at 190°C: (◆) pEH0; (△) bEH15, (○) bEH23, and (□) bEH42.

can also observe the characteristic moduli, G''_{\max} and G_{ν} , from which the values of G_N^0 is extracted [eqs. (2) and (3)]. We have also employed the G'' mechanical dispersion plotted against the natural logarithm of the frequency, as it is shown in Figure 2, to calculate G_N^0 using eqs. (4)–(6). As it can be seen in Table I, the results obtained from the three methods are in convincingly good agreement.

Figure 3(a) shows the values of the plateau modulus as a function of the comonomer mole fraction in the copolymer. The results for other ethylene/ α -olefin copolymers taken from the literature are included for comparison purposes.^{5–7,20,21} These results show the strong effect that comonomer content and type has on the entanglement state. In this context, we have used the packing length model to get an insight on the unperturbed dimensions of the chains.⁸ For a several number of polymers the model has estab-

lished the expression:

$$M_e = 275\rho p^3 \quad (7)$$

where M_e expressed in g/mol, ρ in kg/m³ and p , the packing length, in nm obtained as:

$$p = \frac{M}{\langle R^2 \rangle_0 \rho N_A} = \frac{m_b}{C_\infty l_0^2 \rho N_A} \quad (8)$$

where $M/\langle R^2 \rangle_0$ is the molecular weight to the unperturbed mean square end-to-end distance ratio, N_A is the Avogadro's number, C_∞ is the characteristic ratio (a measure of the stiffness of the chain), and m_b is the average molecular weight per backbone of length l_0 (0.154 nm). We have calculated the characteristic values of p in our materials from Eq. (7), using the values of M_e in Table I. For our samples, we have considered that ρ does not significantly change within the comonomer content range investigated ($\rho = 760$ kg/m³ at 190°C). The comparison of the results obtained in our samples and those from the literature for ethylene/ α -olefin copolymers is observed in Figure 3(b). From eqs. (7) and (8), it is possible to obtain the chain dimensions only from the knowledge of a viscoelastic feature as G_N^0 , and then M_e . The values of the characteristic ratio C_∞ obtained for our materials are listed in Table I. These values are in agreement with recent empirical that suggest a slight variation of the characteristic ratio with $m_b^{-0.30}$ in this range of compositions.⁸ The results indicate that no important differences exist in the stiffness of the chain within this range of comonomer content; then differences observed in viscoelastic features are due to a lose in the chain packing ability [increased p values, as it is observed in Fig. 3(b)].

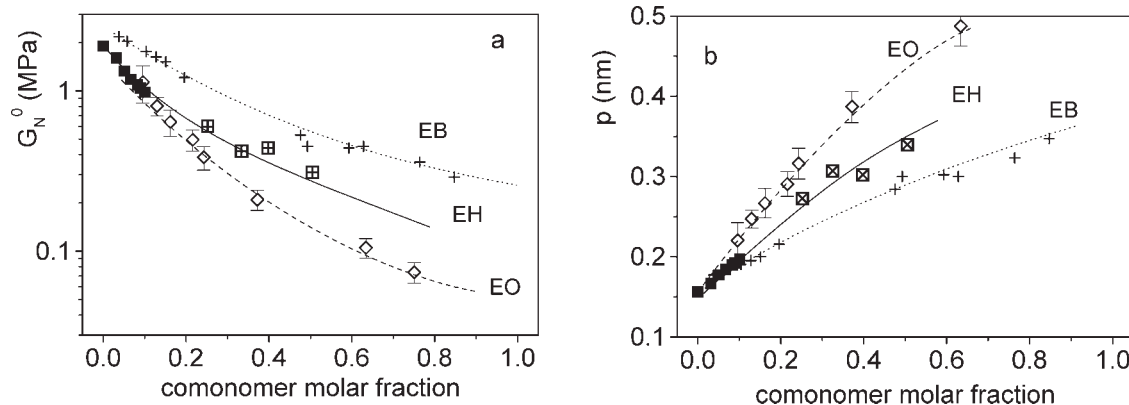


Figure 3 (a) Comparison of the experimental plateau modulus of the ethylene/1-hexene copolymers studied (■) against the values obtained for other ethylene/ α -olefin copolymer from the literature. (◇) ethylene/1-octene (EO) copolymers⁵; (+) ethylene/1-butene (EB) copolymers⁶; (⊗) ethylene/1-hexene (EH) copolymers.^{20,21} The lines are drawn to guide the eye. (b) Packing length versus comonomer content for the same materials than in (a). The values of p has been obtained from Eq. (7).

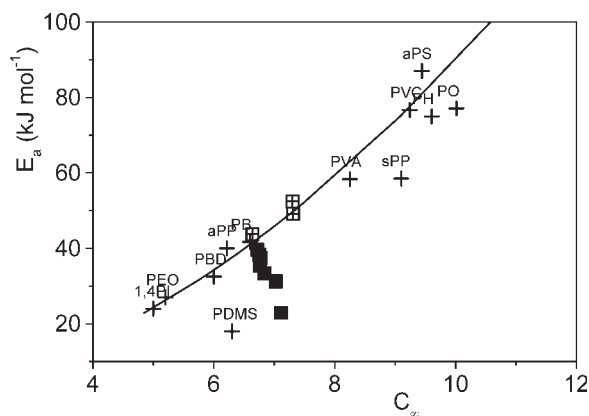


Figure 4 Flow activation energy of the copolymers studied (■) as a function of the characteristic ratio. Results for a several number of homopolymers (+) and ethylene/1-hexene copolymers (⊠) are included. E_a and C_∞ data have been collected from the literature.^{20,21,30,31}

We have also considered the effect of the comonomer content in temperature dependence of the linear viscoelastic properties. In general, the temperature dependence of the relaxation is separated in two different regions above the glass transition temperature. At low temperatures, from T_g to $T_g + 100^\circ\text{C}$, the William-Landel-Ferry,²² or equivalently, the Vogel-Fulcher-Tamman-Hesse equation have to be used^{23–25}:

$$\log a_T = \frac{B(T - T_R)}{(T - T_\infty)(T_R - T_\infty)} \quad (9)$$

being B and T_∞ material dependent parameters. The second region is located at temperatures for $T > T_g + 100^\circ\text{C}$ and follows an Arrhenius dependence:

$$\log a_T = \frac{E_a}{2.303R} \left(\frac{1}{T_R} - \frac{1}{T} \right) \quad (10)$$

The shift factor a_T is defined as $\tau(T)\rho_R T_R / \tau(T_R)\rho T$, where τ is the relaxation time and the subscript R refers to a reference state. The parameter E_a is the so-called flow activation energy, and it depends on chemical composition and architecture.²⁶ In the temperature range studied, a good description of the experimental results is obtained in all the materials by using the Arrhenius dependence given by Eq. (10). The E_a values are listed in Table I for all the materials. It is shown that E_a increases as the molar content of comonomer does. This result is in agreement with the few available data in the literature for ethyl branched polymer models²⁷ and ethylene/ α -olefin copolymers.^{28,29} The seminal works of Schott³⁰ and Porter and Johnson³¹ revealed the influence of polymer chain composition on E_a . In particular, Porter and Johnson observed that the value of E_a increases as a function of the molar volume of side chain

group and the conformational or steric factor, σ . Within this framework, the case of the above-mentioned experimental increase of E_a could be examined by considering the effect of the molar comonomer content on the chain stiffness, since the total molar volume of side chain groups is different in the samples. The results of Porter and Johnson gave rise to the following empirical correlation between E_a and chain stiffness^{31,32}:

$$E_a = 4.3 \exp(4.65 \log \sigma^2) \quad (11)$$

It is possible then to relate E_a with C_∞ , considering $\sigma = (C_\infty/2)^{1/2}$. This expression predicts an increased steric factor, and then C_∞ , as the E_a values increase, and it seems to explain the results obtained for a several number of polymers taken from the literature, as it can be observed in Figure 4.^{20,21,31,32} More recently, Siline and Leonov have developed a statistical model, based on the assumption that the flow activation energy can be related to the size of the basic flow segment. They found a linear relationship between this flow segment, i.e., E_a , and the steric factor for 5 homopolymers.³³

Our samples clearly do not follow the correlation given by Eq. (11). We can see in Figure 4 that the change in the values of E_a is not related to important variations in the chain stiffness in our copolymer series, since the E_a values increases significantly as comonomer content increases, but the values of C_∞ , and then σ , slightly decreases. This later result is in agreement with recent computer simulations in a family of model ethylene/1-hexene copolymers.³⁴ We have to take into account here that the relaxation temperature dependence can also be explained from the concept of free volume.²² Therefore, it is most probably that the expansion coefficient or the glass transition temperature would provide a more general correlation with E_a in this polyolefin series.^{26,35} Unfortunately, the values of the expansion coefficient are not available for our samples yet. Computer simulations based on Monte Carlo algorithms are underway in our group to try to answer some of these questions.

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