

Thermorheological Behavior Analysis of mLLDPE and mVLDPE: Correlation with Branching Structure

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ABSTRACT: In this article, the correlation between the thermorheological behavior and the molecular structure of two grades of metallocene polyethylene, namely linear low density and very low density polyethylene, is studied. The investigated polymers possess the same molecular weight and polydispersity index, but different levels of short branches. Increasing the number of short branches results in enhanced activation energy and delayed relaxation times of the polymers. Four methods including the time–temperature superposition (TTS), van Gurp–Palmen and activation energy (E_a) as a function of the phase angle, $E_a(\delta)$, and the storage modulus, $E_a(G')$ are employed to study the thermorheological behavior of the samples. The results indicated that the thermorheologically simple behavior is dominant in the specimens. Both the $E_a(\delta)$ and $E_a(G')$ showed independency toward phase angle and the storage modulus. Moreover, the activation energy values obtained from the TTS principle and the $E_a(\delta)$ and $E_a(G')$ diagrams were in good agreement. The zero-shear rate viscosity of the samples also followed the equation of the linear polyethylene. Regarding the simple thermorheological behavior and the agreement of the zero shear rate viscosity with the relation of the linear polyethylene, one can conclude that long branches do not exist in the investigated metallocene polyethylenes of this article. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 458–463, 2013

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INTRODUCTION

Studying the thermorheological behavior of polymers as a favorite rheological tool gives us an understanding about molecular structure of polymers such as polyethylenes. Linear viscoelastic properties in different temperatures can be shifted using the time–temperature superposition (TTS) and making the master curve. Time-scale shift factor, a_T can be obtained using the method proposed by Mavridis and Shroff.¹ a_T is expressed by an Arrhenius equation as follows:

$$a_T = \exp\left(\frac{E_a}{R} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \quad (1)$$

where E_a is the activation energy, T the measurement temperature, T_0 the reference temperature and R is the universal gas constant.

The influence of branching (short and long branches) on the rheological properties of polyethylenes has gained much attention during the recent years. The effect of short branches on

rheological properties is mostly considered to be negligible compared to long branches. However, it has been confirmed that short-chain branches affect the temperature dependence of rheological properties. Vega et al.² reported that the activation energy increases with the increase of short-chain branch content.

Activation energy and thermorheological behavior could be different regarding the length of branches in polyethylenes and their molecular structure as well as their branch content. The activation energy of linear polyethylene is reported to be between 26–28 kJ/mol, while slightly higher values (30–34 kJ/mol) is obtained according to the content and kind of comonomer of linear low-density metallocene polyethylenes (mLLDPE).^{3–13}

In literature with incorporating long branches to metallocene polyethylene an increase in the activation energy compared to LLDPE is reported.¹² Also for LDPE which contains a great amount of long branches, activation energy of about 65 kJ/mol is found.¹²

Table I. Characteristics of the Used Materials

Name	M_w (kg/mol)	M_n (kg/mol)	PDI	MFI (g/min)	Density (g/cm ³)	n_c (mol %)	w_c (wt %)
mLLDPE	102.0	40.7	2.5	0.15	0.923	3.3	9.3
mVLDPE	97.3	50.0	2.0	0.16	0.908	6.0	11.3

For linear polyethylene, a simple thermorheological behavior was found, which means E_a is constant. It means that E_a is independent of frequency or modulus and therefore the determined viscoelastic properties in different temperatures can be shifted toward each other to obtain a master curve.^{10,13} A complex thermorheological behavior was also reported about long-chain branched linear low-density metallocene polyethylenes (LCB-mLLDPE) and LDPE which indicates that E_a is related to frequency or modulus. In this case obtaining a master curve was impossible.¹⁰

One of the other ways of studying of the simple and complex thermorheological behavior is van Gorp-Palmen method.¹⁴ Complex thermorheological behavior causes temperature dependence of van Gorp-Palmen (phase angle as a function of complex modulus) curve.^{10–12,14–16} In order to check thermorheological behavior in literature, the curves of the activation energy as a function of storage modulus¹⁰ and phase angle^{10,12} were studied. For LCB-PEs that possessed complex thermorheological behavior, a decrease in activation energy with an increase in storage modulus is reported.¹⁰ Activation energy as a function of storage modulus or phase angle is constant, which is one of the features of simple thermorheological behavior.^{10,12}

This article presents a research on the influence of short-chain branching on thermorheological behavior of molten polyethylene in the linear viscoelastic area. For this purpose, two metallocene polyethylene samples with the same molecular weight and narrow molecular weight distribution with different comonomer content are studied. In order to investigate the thermorheological behavior, several factors (time temperature superposition, van Gorp-Palmen Plots, curves of activation energy as functions of storage modulus and phase angle) were employed and their relationship with the branch structure of the samples are described. Also, there will be a comparison between the different methods. In addition, the relaxation spectrum of samples will be compared. The added value of this contribution is in the fact that several techniques have been combined in order to obtain a consistent picture showing simple thermorheological behavior for m-LLDPE's as well as a dependence of E_a on branch length.

EXPERIMENTAL

Rheological Measurements

Melt rheological linear viscoelastic measurements were carried out with a Paar-Physica Rheometer (MCR300) in the oscillatory shear mode with parallel plates (25 mm in diameter) at a wide frequency range from 0.0.1 to 100 rad/s. A gap of approximately 1 mm was set in all measurements. The measurements were performed at temperature of 130, 150, and 170°C. All experiments were performed under a nitrogen atmosphere. The temperature of the sample, at all measurements, was always maintained

within $\pm 0.5^\circ\text{C}$ of the set temperature. To determine the linear viscoelastic region, strain sweep tests were carried out before starting the frequency sweep measurements.

Materials

The detailed molecular structure of the tested polymers is provided in Table I. The mLLDPE and mVLDPE are provided by ExxonMobil Chemical and the BASF with the commercial names of Exact 3009 [metallocene linear low-density polyethylene (m-LLDPE) with 3.3 mole% hexene as comonomer] and Luflexen 0332H [metallocene very low density polyethylene (m-VLDPE) with 6 mole% butene as comonomer], respectively. These two grades were formerly studied by Razavi Noori et al.¹⁷ The characteristic of these samples is that they have the same molecular weight, M_w , and the similar polydispersity index. In this way, independent of M_w and PDI, one can study the influence of the branches on the melt flow behavior of the samples. For the calculation of the comonomer weight content, w_c , from the comonomer molar content, n_c , the following relation is used,

$$w_c = \frac{n_c \cdot l}{n_c \cdot (l - 2) + 2} \quad (2)$$

where l is the length of the comonomer in numbers of carbon atoms. The weight percentage of the comonomer of each polymer is presented in Table I.

RESULTS AND DISCUSSION

Rheological Characterization

Double-logarithmic plot of the zero-shear viscosity η_0 as a function of the weight-average molecular weight M_w provides a qualitative description of the branch structure of the samples (Figure 1). To determine zero-shear viscosity, Carreau–Yasuda

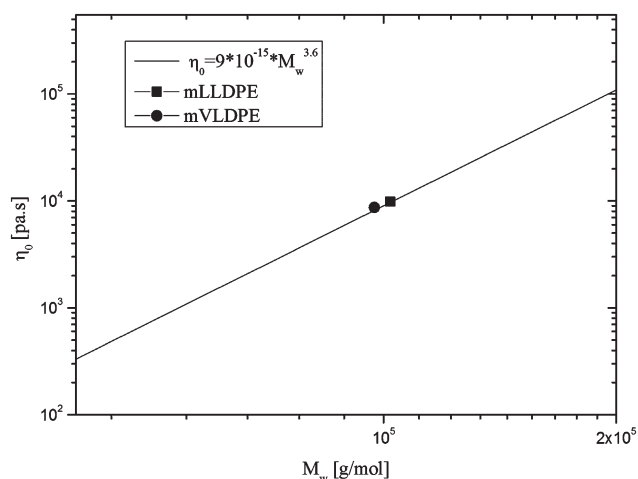


Figure 1. $\eta_0(M_w)$ -plots of mLLDPE and mVLDPE.

Table II. The Values of Parameters in Carreau–Yasuda Equation

Name	η_0	λ	a	n
mLLDPE	9881	0.1125	0.7378	0.1216
mVLDPE	8688	0.1334	0.6367	0.1532

equation^{18–20} is used:

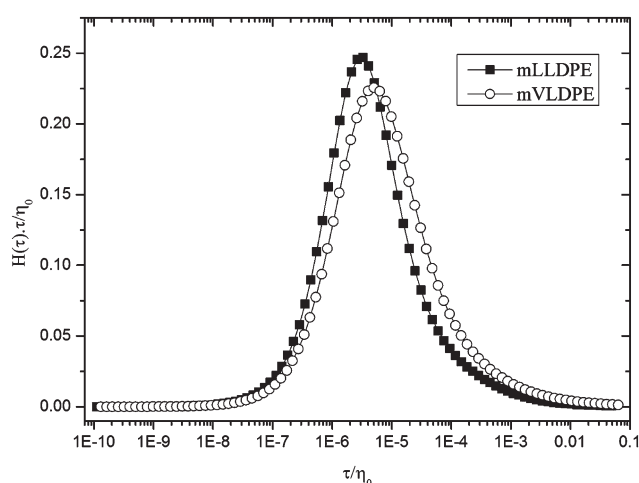
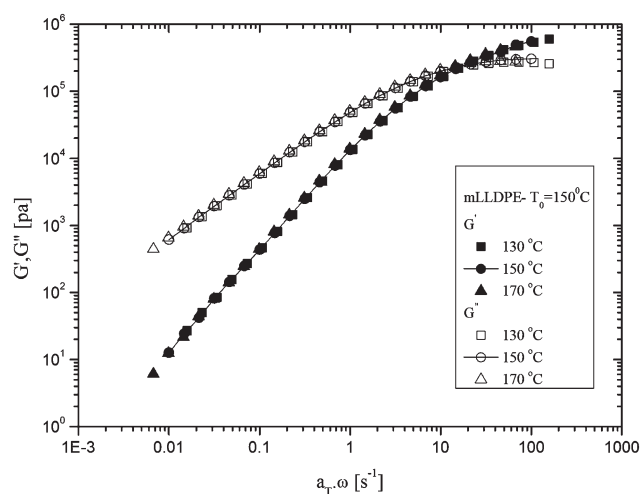
$$|\eta^*(\omega)| = \eta_0 [1 + (\lambda\omega)^a]^{n-1/a} \quad (3)$$

where λ is the characteristic time, “ a ” the width of the transition, $(n - 1)$ is the slope in the shear thinning regime. The values of parameters in Carreau–Yasuda equation for the studied samples are reported in Table II.

Stedler et al.²¹ obtained the following relationship for linear polyethylene between zero-shear viscosity and weight-average molecular weight at 150°C: $\eta_0^{150^\circ\text{C}} = 9 \times 10^{-15} \cdot M_w^{3.6}$ (4)

For substances containing long branches such as LCB-mLLDPE, zero-shear viscosity is located above the reference line (i.e. the line related to linear polyethylene). So the presence of long-chain branches causes a positive deviation from the reference line.¹⁰ According to the literature, the presence of short branches has a slight effect on the zero-shear viscosity.¹² As it is seen the zero-shear viscosity of both samples follows the relationship of linear polyethylene which shows the absence of long-chain branches in the samples. Furthermore, by comparing the characteristic time (λ) of the samples, it is observed that mVLDPE requires further relaxation time compared to mLLDPE.

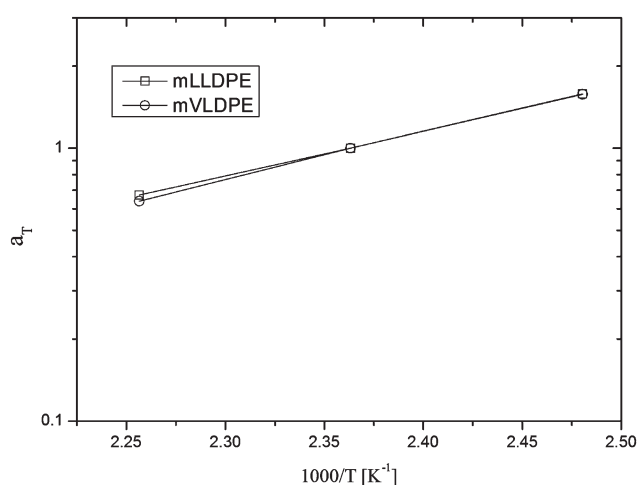
To compare the relaxation behavior of metallocene polyethylene, the weighted relaxation spectra evaluated from the linear viscoelastic data using the US200 software are plotted in Figure 2. It is obvious that mVLDPE shows a longer relaxation time compared to mLLDPE and indicates that mVLDPE contains more branches which require further time for stress relaxation compared to linear chains.

**Figure 2.** Weighted relaxation spectra for mLLDPE and mVLDPE.**Figure 3.** Master curves of G' and G'' for mLLDPE.

Time Temperature Superposition and Determination of the Activation Energy

By employing TTS principle one can establish a quantitative evaluation between the thermorheological behaviors of the samples. Successful application of TTS is usually considered as an indicator of simple thermorheological behavior. In the case of the presence of long branches, master curves can not be constructed successfully and as a result the TTS will fail. For both the studied samples, the simple thermorheological behavior is observed. The double-logarithmic master curves of G' and G'' as a function of $a_T\omega$ are plotted in Figure 3 for mLLDPE. It was possible to find master curves similar to Figure 3 for mVLDPE. As can be observed from Figure 3, successful application of TTS can be considered as an indicator of the absence of long branches.

Activation energies and the a_T values are obtained from the Arrhenius plots of Figure 4. For the mLLDPE and mVLDPE the activation energies are calculated as 31.7 and 33.5 kJ/mol, respectively, which are in accordance with the literature. Since we used only three temperatures for obtaining the linear fits the

**Figure 4.** Arrhenius plots of mLLDPE and mVLDPE.

difference between the activation energies may be regarded to be due to curve fitting errors. However, the coefficient of determination (R^2) values for both of the samples is found to be equal to 0.999, therefore the obtained results are sufficiently accurate and hence the difference in activation energies can be attributed to the difference in branch structures. Of course by using more temperature values, the results will certainly have higher accuracy. As the activation energy is independent of the M_w and the PDI, one can estimate that the greater activation energy of the mVLDPE is because of the higher number of long branches. This enhancement of the activation energy by increasing the portion of the comonomer (augmenting the number of short branches) can be related to the slowed segmental dynamics. The activation energy is representative of the potential energy from the flow of a molten polymer. Introducing the comonomer retards the overall dynamics and consequently higher activation energy is required for the segmental motion.¹³ It is to be noted that in the literature, activation energy values of 26–28 kJ per mole for linear polyethylene have been reported. Activation energy investigated in the current work are of about 5–7 kJ per mole higher than that of linear samples. Therefore this difference can confidently be attributed to the difference in branch structure.

Vega et al.² suggested the following equation to establish a relation between the number of short branches and the activation energy for the copolymers of the ethylene- α olefin (hexane, butane, and octene); the results are confirmed by the FTIR measurement of Mieda et al.²²

$$E_a = 23.8 + 26.7 \times \left[1 - \exp\left(-\frac{n}{35.4}\right) \right] \quad (5)$$

In which n is the number of short branches in each thousand carbon atoms. By using eq. (5), mLLDPE and mVLDPE have 12.5 and 16 short-chain branches in each 1000 carbon atoms, respectively. Since mVLDPE has greater comonomer weight and molar content than that of mLLDPE, it is reasonable that it has also greater amounts of short branches.

Thermorheological Analysis: Van Gorp-Palmen Method

For quantitative study of the thermorheological behavior, the phase angle δ is plotted against the value of the complex modulus $|G^*|$ at different temperatures in Figure 5. In the case of mLLDPE, the diagram is shifted along the G^* axis by multiplying the values in 5 for better visualization. Superposition of the diagrams of the two samples measured at different temperatures represents the simple thermorheological behavior. By using the $\delta(G^*)$ one can interpret the existence of long branches in the polyethylene. In the literature, non-superposition is widely reported for LDPE and LCB-mLLDPE that possess long branches.^{10–12} As a result, in the case of mLLDPE and mVLDPE that successful superpositions were obtained, one can conclude that long branches are not present in these polymers.

Other Methods for Thermorheological Analysis

To evaluate the thermorheological behavior in greater details, one can use the activation energy curves as functions of phase angle (δ) according to Kessner and Munstedt method¹⁰ and as a function of the storage modulus (G') based on Wood-Adams and Costeux method.⁴

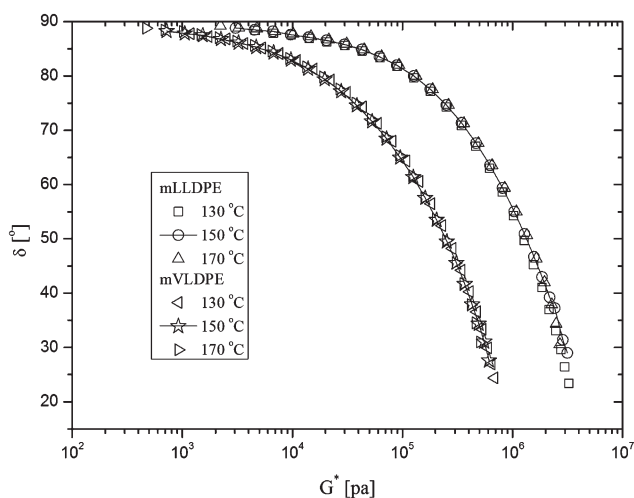


Figure 5. $\delta(G^*)$ -plots of mLLDPE and mVLDPE. mLLDPE is shifted by the factor of 5 along the modulus axis for the matter of a better visualization.

Thermorheological Analysis: $E_a(\delta)$ According to Kessner and Munstedt Method

Regarding Kessner and Munstedt method the logarithms of the time-scale shift factors at a constant δ are plotted versus the reciprocal absolute temperature $1/T$ [Figure 6(a) and (b)], and by using the Arrhenius relationship for shift factors, the activation energies for m-PEs are plotted as a function of δ in Figure 7. Both samples show that the activation energy is constant in this curve. This is the result that Kessner et al.^{10,12} reported for linear polyethylenes. They also reported the dependence of activation energy on δ for LDPE and LCB-mLLDPE and attributed this to the presence of long-chain branches. So it can be concluded from this curve that long-chain branches do not exist in the studied samples.

Thermorheological Analysis: $E_a(G')$ According to Wood-Adams and Costeux Method

Figure 8 shows the activation energy of m-PEs as a function of storage modulus according to Wood Adams and Costeux method. To obtain the values, in several G' s measured in different temperatures, shift factors were obtained and then the activation energies were determined from the temperature dependence of these shift factors. Kessner and Munstedt¹⁰ observed an activation energy for long-chain branched polyethylenes that is dependent on the modulus which shows the complex thermorheological behavior. For both the studied m-PEs the activation energy is constant and independent of storage modulus, which reflects thermorheological simplicity and is confirmed with the conclusion that was obtained before.

The average activation energy values which were obtained from Figures 7 and 8 are shown in Table III. As it is seen from Table III there is a good agreement between the gained activation energy from these two methods and the activation energy which was obtained from the shift factor related to the TTS principle.

CONCLUSION

For both of the metallocene polyethylenes in this study the zero-shear rate viscosity follows the equation of the linear

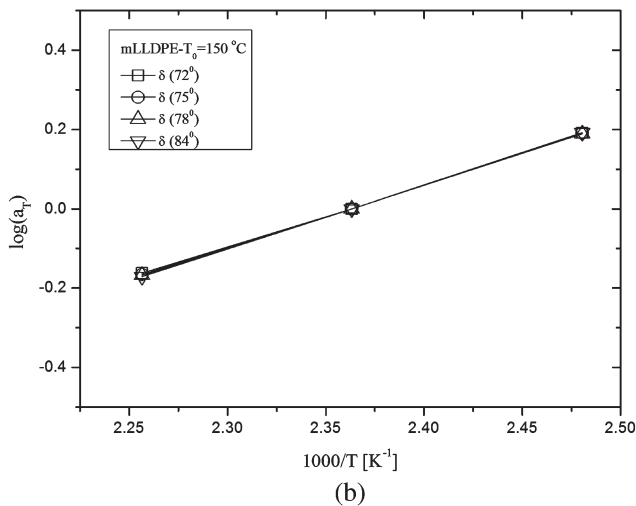
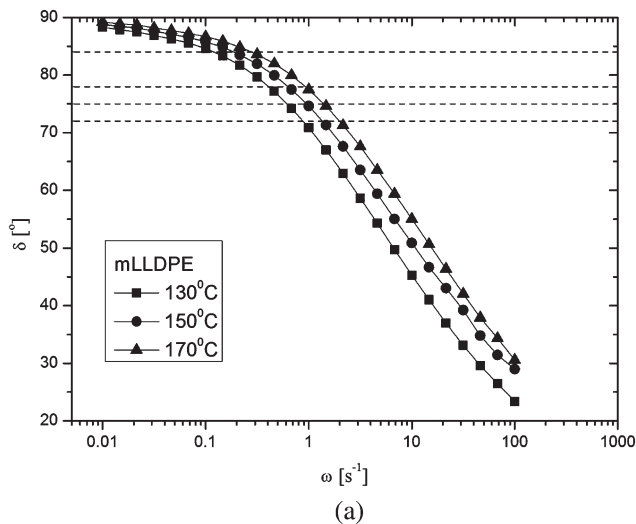


Figure 6. (a) Characteristics of δ as a function of ω at different temperatures for mLLDPE. (b) Arrhenius-plots of the shift factors for various phase angles.

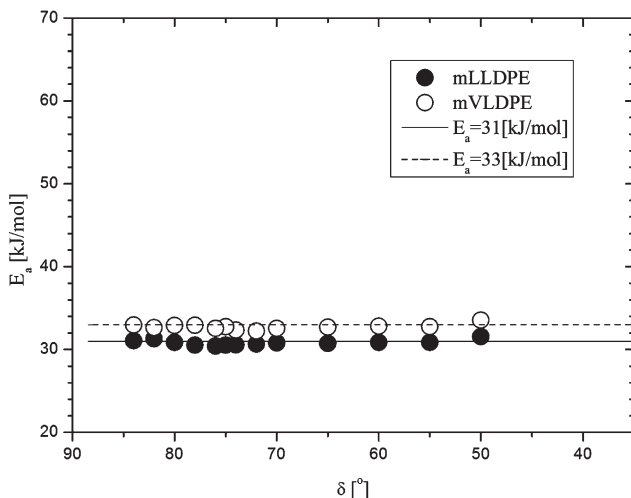


Figure 7. Activation energies as a function of the phase angle for mLLDPE and mVLDPE.

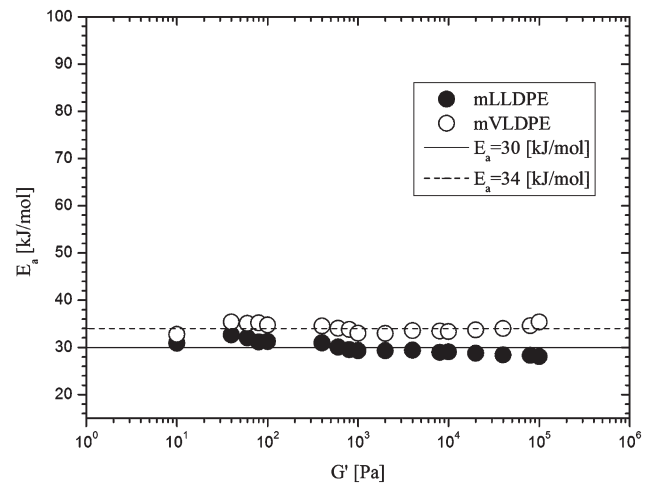


Figure 8. Activation energies as a function of the storage modulus for mLLDPE and mVLDPE.

polyethylene. By comparing the relaxation spectra of the samples (and also the characteristic relaxation times obtained from Carreau–Yasudaw), it was found that mVLDPE has a longer characteristic relaxation time. Considering the same molecular weight and the polydispersity index of the samples, the longer relaxation time is due to the greater number of the branches of the mVLDPE in comparison to the mLLDPE. The TTS was valid for the specimens and the master curves were successfully constructed. In the case of van Gorp–Palmen diagram, no complex thermorheological behavior was observed. The activation energy diagrams as a function of storage modulus and phase angle resulted in constant activation energy independent of the storage modulus and phase angle. Employing four methods including the TTS, van Gorp–Palmen, activation energy as a function of phase angle, and the storage modulus the simple thermorheological behavior was observed. Considering the simple thermorheological behavior and the agreement of the zero shear rate viscosity with the relation of the linear polyethylene, it can be concluded that no long branch exists in the molecular structure of the mLLDPE and mVLDPE. The calculated activation energy of mLLDPE and mVLDPE which are 31.7 and 33.5 kJ/mol are in good agreement with the values reported in the literature. In addition, the greater activation energy of the mVLDPE is a result of its higher number of short branches in comparison to mLLDPE. The activation energy values reported from the $E_a(\delta)$ and $E_a(G')$ are in good agreement, confirming the validity of these methods in evaluating the thermorheological behavior. Finally, it can be claimed that studying the

Table III. Activation Energy Values for mLLDPE and VLDPE

Name	E_a^a (kJ/mol)	E_a^b (kJ/mol)	E_a^c (kJ/mol)
mLLDPE	31.7	30.9	30
mVLDPE	33.5	32.8	33.9

^a E_a obtained from TTS method.

^bAverage E_a obtained from Kessner and Munstedt method.

^cAverage E_a obtained from Wood-Adams and Costeux method.

thermorheological behavior can be considered as a powerful rheological method in investigating the molecular structure of polymers.

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