

# Influence of Molecular Structure on the Rheology and Thermorheology of Metallocene Polyethylenes

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**ABSTRACT:** The rheology of linear and branched metallocene polyethylenes (m-PEs) was investigated. The linear metallocenes were prepared by gas-phase polymerization, while the branched PEs were commercial resins. Molecular parameters such as  $M_w$ , branch type, and molecular weight distribution have influenced the viscoelastic behavior of both linear and branched PEs, whereas branch content (BC) had little influence on viscoelastic properties. Plots of  $\log G'$  versus  $\log G''$  revealed the effect of comonomer type on the viscoelastic behavior of m-PEs. Flow activation energy ( $E$ ) was found to be sensitive to both  $M_w$  and BC. Also,  $E$  for

ethylene-octene copolymers was observed to be always higher than the butene counterparts, which have been caused by the increase in molar volume of the repeating unit. For the effect of BC on  $E$ , different trends were observed for octene and butene m-LLDPEs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1717–1728, 2006

**Key words:** branch content; comonomer type; molecular weight; thermorheology; activation energy; metallocene polyethylene

## INTRODUCTION

Molecular architecture is known to have a strong influence on the solution, melt, and solid state properties of polyethylenes (PEs).<sup>1–13</sup> Attempt for controlled synthesis of PEs has been a very hot activity since the discovery of this material. A good review on the subject is given elsewhere.<sup>1,2</sup> Molecular structure has been documented to affect both the processing and end-use properties.<sup>3–13</sup> Molecular parameters such as  $M_w$ , molecular weight distribution (MWD), short chain branching (SCB), long chain branching (LCB), distribution of branches, and type of branching (comonomer type) all have been found to affect the rheological and solid state properties.<sup>3–8,10–13</sup> Linear low density PE (LLDPE) is a copolymer of ethylene and an  $\alpha$ -olefin such as butene, hexene, or octene. They were first produced by Ziegler–Natta (ZN) heterogeneous catalyzes, whose origins can be traced back to the late 1950s.<sup>2</sup> Many studies that previously examined the influence of molecular architecture used ZN-PEs.<sup>11,13,14–16</sup> However, these LLDPE resins are known for their compositional heterogeneity. The occurrence of fairly complex comonomer distributions is a basic attribute of Ziegler–Natta LLDPE (ZN-LLDPE) resins.

Temperature rising elution fractionation (TREF) of these copolymers revealed that one could obtain two or three regimes within the comonomer distribution (high, medium, and very low density).<sup>16,17</sup> The development of single site catalysts have made possible the synthesis of PEs with controlled architecture. These polyolefins are catalyzed with what are alternatively called metallocene, or single site catalysts, and have uniform comonomer distribution and narrow MWD. More recent studies appearing on the structure–property relationships have used these PEs.<sup>3,4,7,9–12</sup> A very important aspect in these investigations is the isolation of the interaction of molecular parameters controlling a specific property. This could not be achieved by ZN-LLDPEs.

Wood-Adams et al.<sup>3</sup> carried out a detailed investigation on the influence of  $M_w$ , MWD, and SCB on the linear viscoelastic behavior of *m*-PEs that had LCB. Linear as well as branched PEs was studied. An increase in  $M_w$  was reported to cause an increase in zero-shear viscosity ( $\eta_0$ ) and decrease in the shear rate at which shear thinning begins. The  $\eta_0(M_w)$  data was successfully fitted to an expression  $\eta = KM_w^\alpha$ ; with  $K = 6.8 \times 10^{-15}$  (Pa s/[g/mol]<sup>3.6</sup>) and  $\alpha = 3.6$ . On the other hand, increasing the MWD distribution was reported to broaden the transition zone between Newtonian plateau and the power law zone. Interesting observations were made regarding the influence of LCB on the viscoelastic behavior of PEs. Increasing

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TABLE I  
Characterization of Polyethylene Resins

Sample ID	Resin Type	Branch Type	$M_w$ (kg/mol)	MWD	BC CH <sub>3</sub> /1000 C	Density (g/cm <sup>3</sup> )	MI g/10 min
LM1	m-HDPE	–	160	2.35	0	N/A	N/A
LM2	m-HDPE	–	169	2.17	0	N/A	N/A
LM3	m-HDPE	–	155	2.07	0	N/A	N/A
HDPE	HDPE	–	101	6.71	0	0.9610	0.70
EB15	m-LLDPE	Butene	108	1.95	14.5	0.9100	1.20
EB19	m-LLDPE	Butene	110	1.78	18.5	0.9000	1.20
EB42	m-LLDPE	Butene	125	1.81	42	0.8800	0.80
EB45	m-LLDPE	Butene	62	2.01	45	0.8800	10
EO15	m-LLDPE	Octene	84	1.47	15.9	N/A	N/A
EO16	m-LLDPE	Octene	90	2.04	16.3	0.9020	1.10
EO19	m-LLDPE	Octene	74	2.10	18.7	0.9020	3.00
EO26	m-LLDPE	Octene	75	1.40	25.9	0.8820	1.1
EO33	m-LLDPE	Octene	95	1.99	32.7	0.8820	1.1

LCB increased  $\eta_0$ , degree of shear thinning, and broadened the transition zone between Newtonian plateau and the power law zone. So, the effect of LCB is equivalent to the combined effects of  $M_w$  and MWD. However, no influence of short chain branching was observed on the viscoelastic behavior of PEs. Kim et al.<sup>5</sup> also reported little influence of short chain branching on the rheological properties of PE melts that had LCB. Lin et al.<sup>6</sup> studied the influence of side-chain structures on the viscoelastic behavior of PEs. However, the interaction of molecular parameters was not isolated. The PEs used in the study had different  $M_w$  and BC. They reported that Cole-Cole plots ( $\log G'$  versus  $\log G''$ ) can qualitatively characterize the effects of the side chains on the melt rheological properties of PEs. In another study, the influence of  $M_w$  and MWD on the viscoelastic and processing behavior of ZN-PEs with focus on melt fracture was investigated.<sup>4</sup> It was found that increasing MWD increases the zero shear viscosity, flow activation energy, degree of shear thinning, and extrudate swell. On the other hand, the increase in  $M_w$  increased the apparent melt viscosity and extrudate swell but decreased the shear stress for the onset of melt fracture. Flow activation energy was found to decrease with  $M_w$ .

The temperature dependence of the viscosity of amorphous polymer melts, at temperatures far enough above the glass transition ( $T > T_g + 100$ ), follows a simple Arrhenius-type relationship:

$$\eta = Ae^{E/RT} \quad (1)$$

where,  $E$  is the activation energy for viscous flow,  $R$  is the gas constant, and  $A$  is a constant. This expression was first formulated for low- $M_w$  liquids by Andrade.<sup>18</sup> Eyring and coworkers<sup>19,20</sup> interpreted this equation with the aid of their hole theory of liquids. In polymers, however,  $E(M_w)$  levels at quite low  $M_w$ ,<sup>19</sup> which means that in long chains (like linear PE) the segment of flow

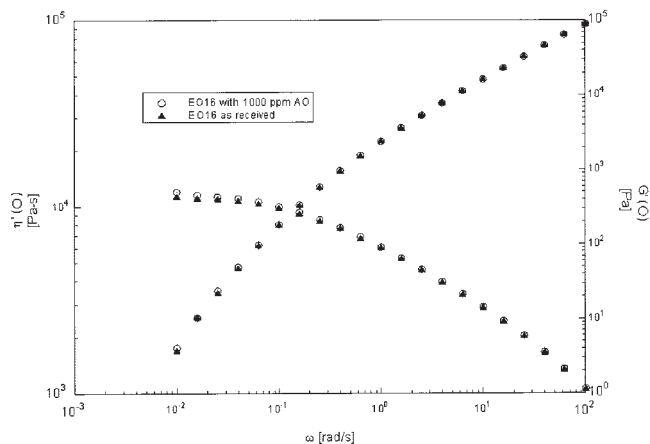
(20–25 backbone carbon atoms) is considerably smaller than the complete molecule. The estimated activation energy of flow for such a unit was 6–7 kcal (25–29 kJ/mol), in excellent agreement with the viscometrically measured activation energies for HDPE.<sup>16,21,22</sup>

In this study, we would like to investigate the effect of molecular parameters such as  $M_w$ , MWD, BC, and comonomer type on the linear rheology of linear and linear low density m-PEs. To avoid the usual molecular interactions encountered in ZN-PEs, metallocene PE samples were selected and grouped such that they mainly differ in a single molecular parameter. As a result, the comparison of the rheology of each group will reveal the effect of that particular parameter on the viscoelastic behavior. Further, the thermorheology of these polyolefins was investigated by computing the flow activation energies. The influence of molecular architecture on flow activation energy is also examined.

## EXPERIMENTAL

### Materials and characterization

Nine different grades of m-LLDPE [4 ethylene–butene (EB); 5 ethylene–octene (EO)], and one linear ZN-HDPE were obtained from ExxonMobil, Belgium. In addition, three linear metallocenes were specially synthesized and characterized by Professor S.E. Wanke of the University of Alberta. All linear metallocene (LM) were nascent samples, i.e., these samples as were removed from the reactor; no additives have been added. The LM samples were prepared by gas-phase polymerization. Laboratory prepared catalysts were used for all the polyethylene synthesis. The catalyst was  $(n\text{-BuCp})_2\text{ZrCl}_2$  on polymeric support treated with MAO. The reactor pressure was 200 psi and hydrogen was used for samples LM1 and LM2. The reactor temperature is 60, 60, and 70°C for samples LM1 to LM3, respectively. Details of the resins are



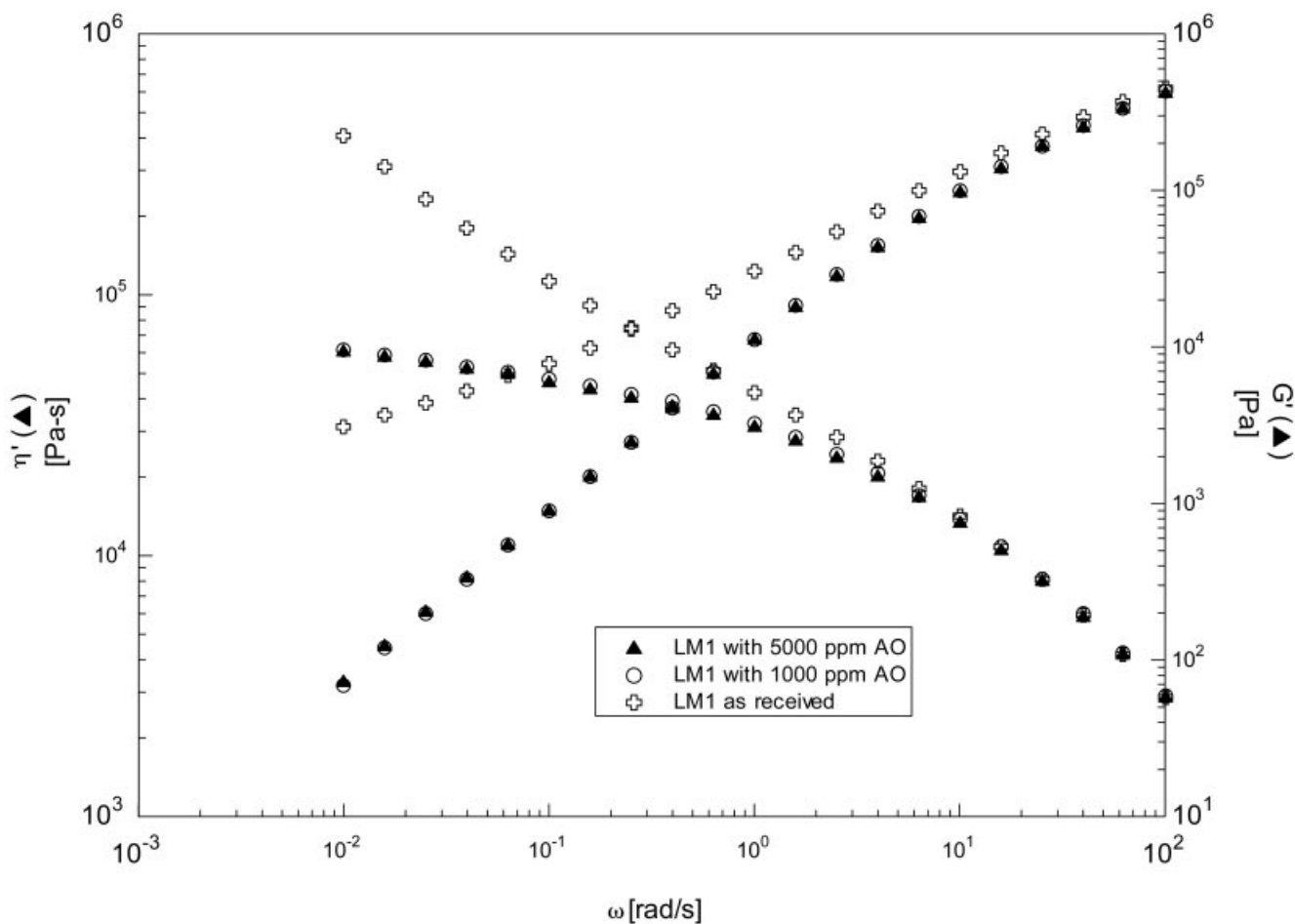
**Figure 1**  $\eta'(\omega)$  and  $G'(\omega)$  for EB16 ( $T_{\text{test}} = 190^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

presented in Table I. The EB and EO resins covered a wide range of branch content as shown in Table I. Branched PE samples were named according to their branch type and content. For example, sample EB15 means the LLDPE is a metallocene copolymer of eth-

ylene and butene with an average branch content of  $\sim 15$   $\text{CH}_3/1000$  C. Similarly, EO33 is a metallocene copolymer of ethylene and octene with an average branch content of  $\sim 33$   $\text{CH}_3/1000$  C.

The weight-average molecular weights as well as molecular weight distribution (MWD) were obtained by gel permeation chromatography (GPC). GPC data was collected using 1,2,4 trichlorobenzene as solvent at  $150^\circ\text{C}$  in a WATERS GPC2000 instrument. Polystyrene and polyethylene standards were used for calibration. In addition, all the LLDPE samples were characterized by  $^{13}\text{C}$  NMR for branch content ( $\text{CH}_3/1000$  C). Details of the characterization results are presented in Table I.

Normally, 0.1% (1000 ppm) or less of primary and secondary antioxidants (AO) are used commercially for polyolefin stabilization.<sup>23</sup> Here, adequate amount of extra AO mixture were added to all resins used in this study before melt conditioning in a Haake PolyLab blender when needed. Details on the determination of the adequate amount needed to avoid degradation are discussed elsewhere.<sup>24</sup> The extra AO was a 50/50 blend of Irganox 1010 and Irganox 168. Both antioxi-



**Figure 2**  $\eta'(\omega)$  and  $G'(\omega)$  for LM1 ( $T_{\text{test}} = 190^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

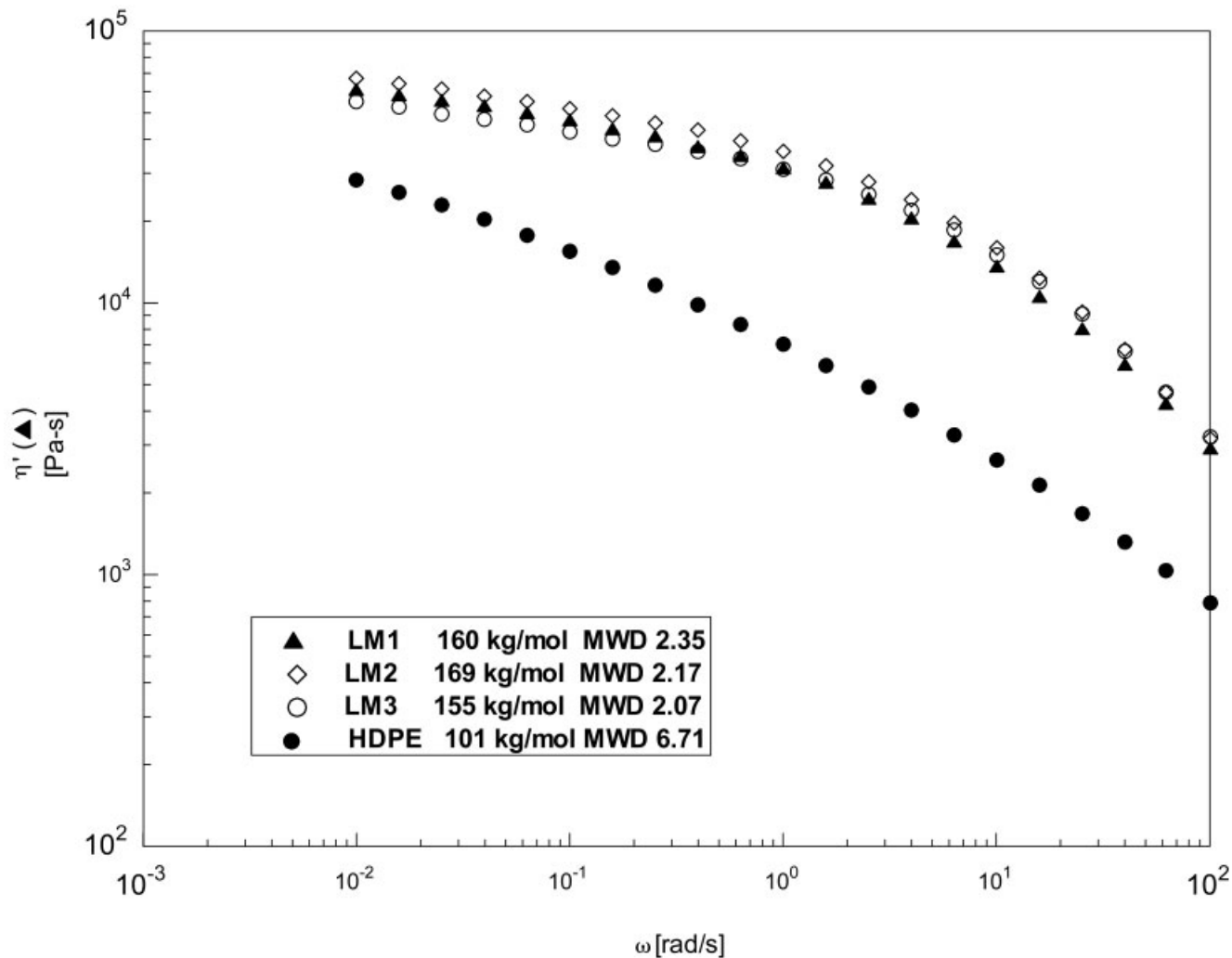


Figure 3  $\eta'(\omega)$  for linear LM1, ML2, LM3, and HDPE ( $T_{\text{test}} = 190^{\circ}\text{C}$ ;  $\gamma^{\circ} = 15\%$ ).

dants were obtained from Ciba Specialty Chemicals, Switzerland.

### Rheological testing

In all cases, the PE samples were given a controlled thermomechanical history in a melt blender before introduction into the rheometer for shear testing. The melt blender is designed for use as a computer-controlled torque rheometer, which can also be operated as an extruder or as a mixer. The latter configuration, featuring a sample bowl containing 60 mL of melt, was used for conditioning different polymers at constant temperature, rotor speed, and for a fixed time. The linear and branched PE resins used in this study were conditioned in the melt blender at 50 rpm and  $190^{\circ}\text{C}$  for 10 min. "Pure" polymers were conditioned in the presence of adequate amounts of extra AO. The "conditioned" samples were then removed from the mixing bowl and air-cooled. In some cases, as-received resins were prepared and used for comparison purposes. Specimens for

rheological testing were prepared from melt-blended (or as-received) resin(s) by molding discs, about 2 mm thick, designed to match the platen diameters employed in the rheometer; this process was carried out in a Carver hydraulic press. The ARES rheometer (TA Instruments) was used to study linear rheological properties as functions of sinusoidal frequency ( $\omega$ ) and temperature ( $T$ ). Flow activation energy,  $E$ , was measured for the resins in an attempt to correlate  $E$  to  $M_w$  and BC. All dynamic shear testing was carried out using the cone and plate geometry, and strain amplitude ( $\gamma^0$ ) of 15% was selected following  $\gamma$ -sweep test. All tests were performed under a nitrogen blanket. In temperature sweep tests, a tool thermal expansion coefficient of  $3 \mu\text{m}/^{\circ}\text{C}$  was used.

## RESULTS AND DISCUSSION

### Degradation of m-PEs

The first part of this study examined the possibility of degradation of PEs during the melt blending process.

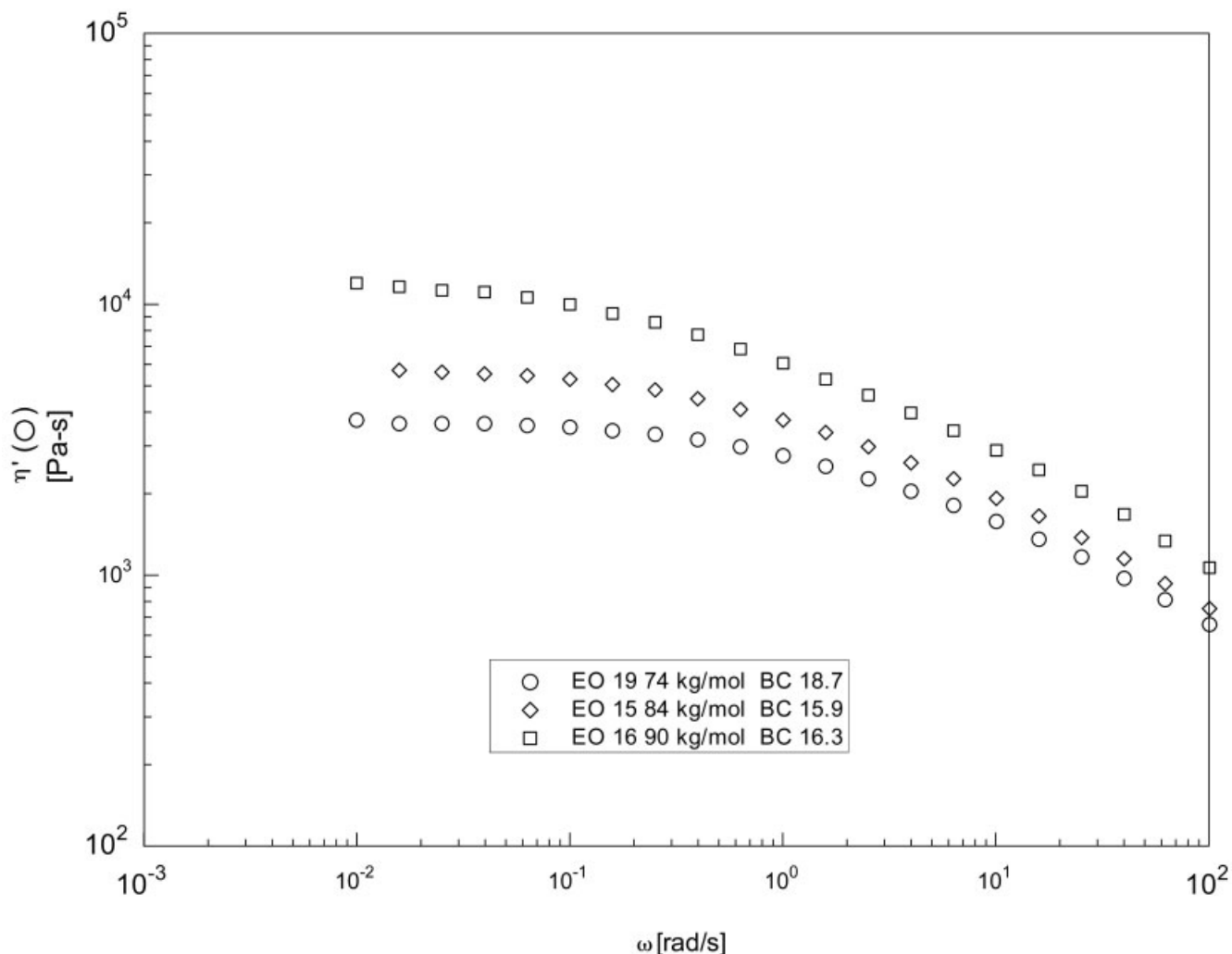


Figure 4  $\eta'(\omega)$  for branched EO15, EO16, and EO19 ( $T_{\text{test}} = 190^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

Rheology was used to monitor the structural modification of PEs during the conditioning process and the adequate amount of antioxidant (AO) was added accordingly. Frequency sweep testing (0.01–100 rad/s) was employed rather than steady shear to avoid any sample modifications that could result from the large strains inherent in the latter.

Figure 1 displays the  $\omega$ -sweep test results for EB16 conditioned at  $190^\circ\text{C}$  with additional AO (1000 ppm). The results are compared with the corresponding values for the as-received resin tested at the same temperature. The dynamic viscosity measurements,  $\eta'(\omega)$ , and storage modulus,  $G'(\omega)$ , showed excellent agreement between results obtained for the as-received (control sample) and conditioned samples, suggesting that the presence of extra AO protected the conditioned resin from degradation. The excellent agreement of  $\eta'(\omega)$  and  $G'(\omega)$  for the two samples also serves as a check for the reproducibility of our data.

Results for frequency sweeps tests for LM1 (a representative linear metallocene resin) are shown in Fig-

ure 2. LM1 was a nascent resin sample and hence did not contain any AO. At low- $\omega$ , as-received LM1 showed a very strong yield stress behavior, which is not typical of linear m-PEs with no LCB. Hence, degradation was suspected and the sample was conditioned in the presence of 1000 as well as 5000 ppm AO. Results for the conditioned resins with extra AO showed a major drop in both viscoelastic properties such as  $\eta'(\omega)$  and  $G'(\omega)$ . The viscoelastic properties overlaid for both samples containing 1000 and 5000 ppm AO, demonstrating that 1000 ppm was sufficient to protect the resin from degradation. The presence of small amount of AO caused the rheology of the conditioned resins to show the typical Newtonian plateau in the viscosity curve. This suggests that nascent metallocene resins are sensitive to degradation and extra amounts of AO should be added.

Similarly, the comparison of dynamic shear rheology of as-received and conditioned resins was performed for other samples (results not shown) and appreciable amounts of AO was added whenever needed.

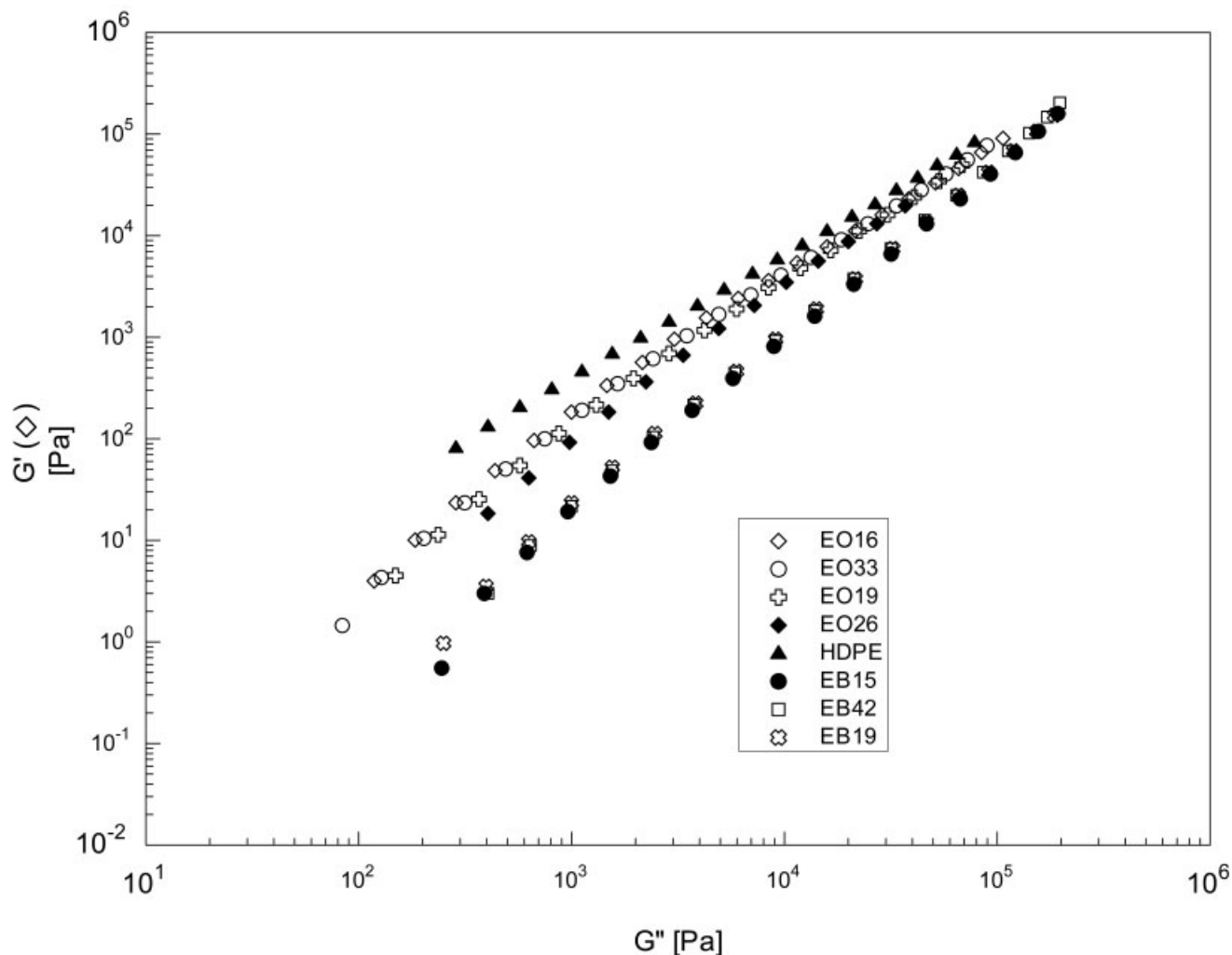


Figure 5  $G'$  versus  $G''$  for branched PEs ( $T_{\text{test}} = 190^{\circ}\text{C}$ ;  $\gamma^{\circ} = 15\%$ ).

#### Influence of $M_w$ , branch type, and branch content on the rheology of m-PEs

Figure 3 shows the dynamic viscosity data for linear PEs used in this study. Samples LM1, LM2, LM3, and HDPE are all linear m-PE resins and differ only in  $M_w$ . Hence, the comparison will reveal the influence of  $M_w$  on the linear viscoelastic properties of these polymers. Because of the high  $M_w$  of these polymers we did not observe very clear Newtonian plateau at  $190^{\circ}\text{C}$  in the range  $\omega = 0.01\text{--}100\text{ s}^{-1}$ . However, the trend in viscosity change with  $M_w$  is very clear. An increase in  $M_w$  caused an increase in viscosity at low- $\omega$  in agreement with the previous reports.<sup>3,4,8</sup> Since we could not attain Newtonian plateaus in the range studied, it is difficult to have conclusive results about the onset of shear thinning. However, the effect of MWD is very clear. The three metallocene samples LM1, LM2, and LM3 have very narrow MWD of  $\sim 2$ ; hence they exhibit similar shear thinning behavior. On the other hand, the commercial HDPE sample, which has a very high MWD (MWD = 6.7), showed a very different

behavior. This sample shows almost no plateau and exhibits a pronounced shear-thinning behavior. It is difficult to see any transition zone between the Newtonian and the power-law zone. So, the effect of MWD is in agreement with earlier reports regardless whether the m-PEs had LCB or not.<sup>3,4</sup>

Figure 4 shows the influence of  $M_w$  on the linear viscoelastic properties of branched PEs. The three LLDPE (EO19, EO15, and EO16) are octene copolymers synthesized from metallocene catalysts. They have close branch contents and narrow MWD, hence the dominant factor influencing the rheology is  $M_w$ . Unlike the linear PEs, a typical Newtonian plateau is observed for m-LLDPEs, which extends over almost a decade. At low- $\omega$ , the viscosity increases with the increase in  $M_w$ , the same trend was observed for the linear m-PEs. However, the differences in viscosities are much larger for branched PEs from their linear counterparts. Further, it could be easily seen that the frequency that corresponds to the onset of shear thinning decreases with the increase in  $M_w$  in conformity

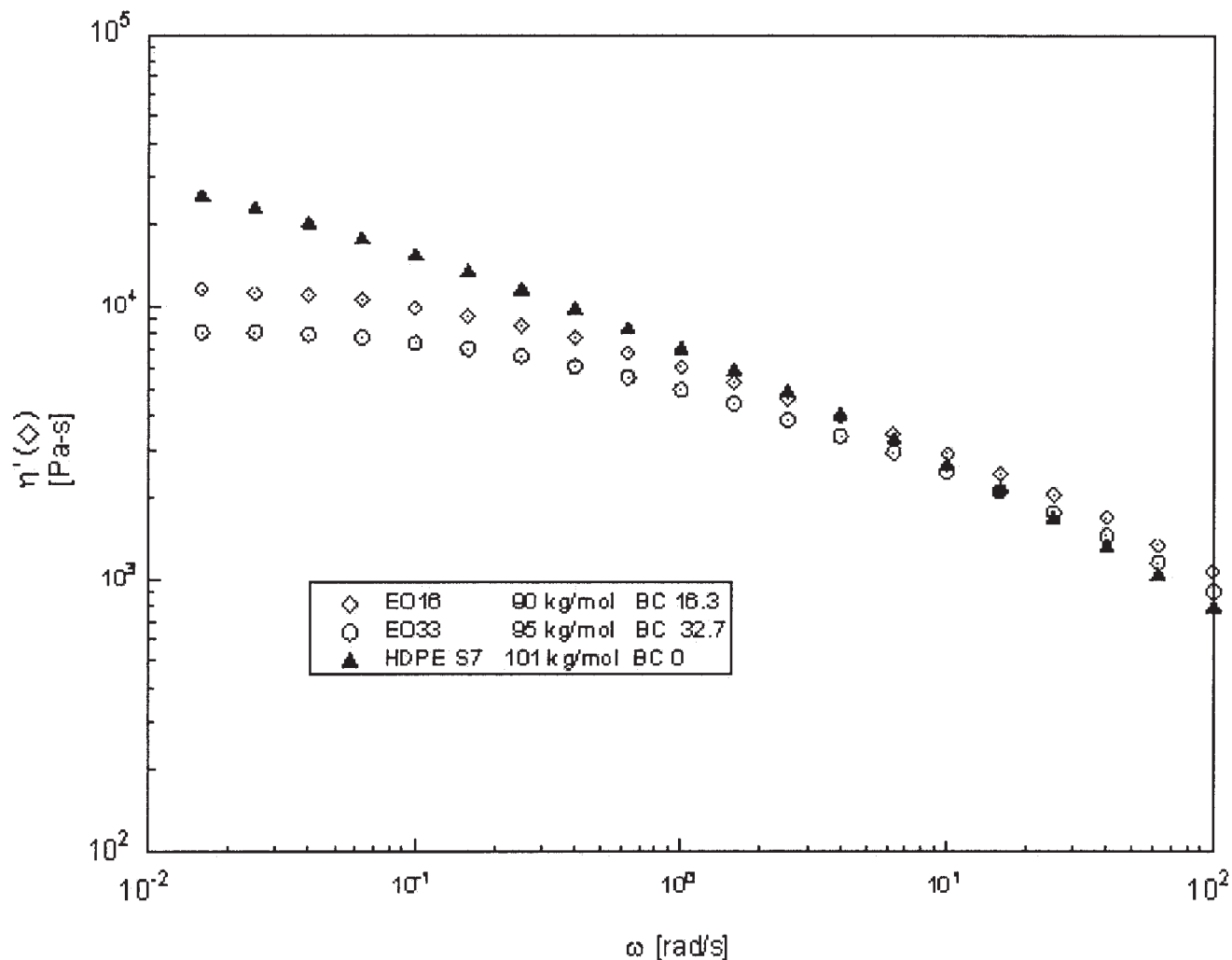


Figure 6  $\eta'(\omega)$  for EO16 and EO33 ( $T_{\text{test}} = 190^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

with previous reports.<sup>3,4</sup> This frequency corresponds to the largest relaxation time,  $\lambda_0$ .

For polymeric systems, plots of  $\log G'$  versus  $\log G''$  have been used to study effects of LCB, polydispersity, blend miscibility, and molecular architecture.<sup>6,8,25-28</sup> Lin et al.<sup>6</sup> have reported that  $\log G'$  versus  $\log G''$  can qualitatively define the effects of side chain branching on the rheological properties of polymer melts. To further explore the influence of the molecular architecture on the viscoelastic behavior,  $\log G'$  versus  $\log G''$  plots for HDPE, metallocene catalyzed EO, and EB are presented in Figure 5. Curves for EO and EB with different BC and  $M_w$  could be adjusted to two single lines of overlapping curves. However, it is very interesting to observe that the two lines do not overlap. It has been reported that  $\log G'$  versus  $\log G''$  curves for polydisperse and presumably long chain branched samples deviate from those of narrow MWD and short branched samples, which can be adjusted to a single line.<sup>8</sup>

All EB and EO samples used in this study are metallocene m-PEs with narrow MWD (1.4–2.10) and no

LCB. The ExxonMobil technology used to produce these resins does not include LCB like the Dow Insite technology.<sup>3</sup> However, the interesting part is that EO and EB resins do not fall on the same line. We stress that this could be an effect of branch type (octene versus butene). The two sets of samples have narrow MWD and do not contain any LCB so the difference in behavior could only be a consequence of comonomer type. Such an observation has not been reported before in the literature. Vega et al.<sup>8</sup> used only hexene-ethylene copolymers, while Lin et al.<sup>6</sup> did not isolate the effects of different molecular parameters. The effect of MWD is very obvious in the case of HDPE curve (MWD 6.7) lying in the upper left corner. Hence, the branch type has an effect on the viscoelastic behavior.

Furthermore, the effect of BC on the viscoelastic properties of EO16 and EO33 was compared. Once again, HDPE is shown as a reference linear PE (see Fig. 6). As discussed earlier, the dominant factor influencing rheology is BC, since all other parameters are similar. The zero shear viscosity is observed to de-

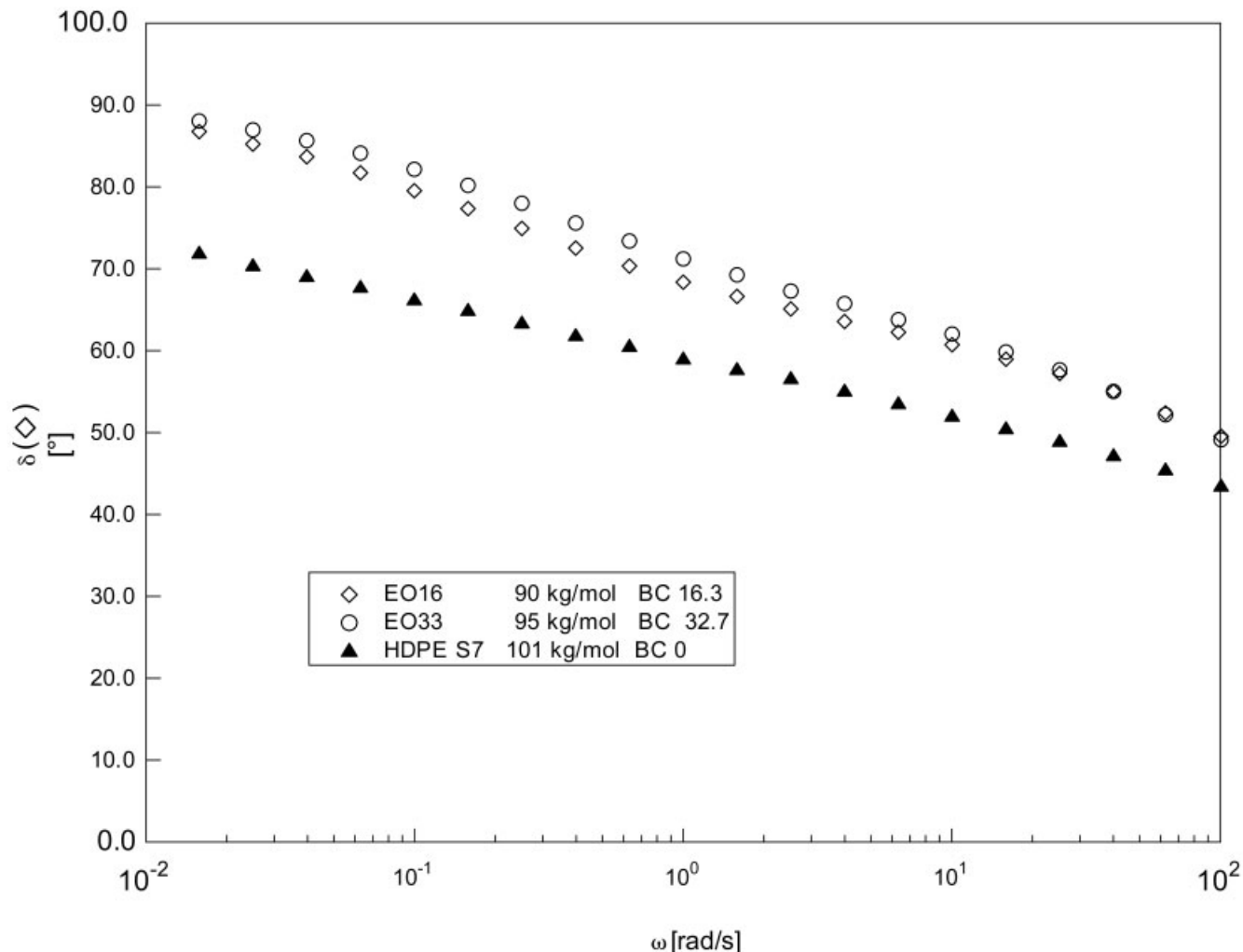


Figure 7  $\delta^0(\omega)$  for EO16 and EO33 ( $T_{\text{test}} = 190^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

crease a little with the increase in branch content, otherwise the behavior is comparable. The effect of BC on loss angle ( $\delta^0$ ) is presented in Figure 7. The behavior of the two resins is quite similar. The little differences in the transition zone could be due to the minute differences in MWD of the two resins. Our results for octene m-LLDPEs are similar to those reported for butene copolymers earlier.<sup>3</sup>

The influence of  $M_w$  on the  $\eta_0$  has been a subject of many investigations.<sup>3,4,8</sup> When  $\eta_0$  was plotted against  $M_w$  on a log-log scale, different values for the slope 3.4,<sup>29</sup> 4.1,<sup>4</sup> and 3.6<sup>3,8</sup> have been reported in the literature. To get zero shear viscosities, the dynamic shear viscosity,  $\eta'$ , data for linear and branched polyethylene samples was fitted to Carreau ( $\eta = \frac{\eta_0}{[1 + (\lambda\omega)^{m_1}]^{m_2}}$ ). Model parameters such as zero-shear viscosity,  $\eta_0$ , and relaxation time,  $\lambda$ , are given for different linear and branched resins in Table II. In some cases,  $\eta_0$  could not be obtained since no Newtonian plateau was observed. In general, the EO resins

showed higher values of  $\lambda$  in comparison to the EB resins. This could be attributed to the influence of branch length on the shear thinning behavior of these resins. Figure 8 shows  $\eta_0$  as function of  $M_w$  for linear and branched polyethylene samples. The data for the

TABLE II  
Parameters of Carreau Model (in Terms of  $\omega$ )

Sample ID	$M_w$ (kg/mol)	MWD	$\eta_0$ (Pa s)	$\lambda$ (s)
LM1	160	2.35	65572	0.039
LM2	169	2.17	69161	0.026
LM3	155	2.07	50340	0.040
HDPE	101	6.71	—	—
EB15	108	1.95	7413	0.018
EB19	110	1.78	7614	0.021
EB42	125	1.81	12231	0.023
EO15	84	1.47	6724	0.757
EO16	90	2.04	12955	1.69
EO19	74	2.10	4421	1.00
EO26	75	1.40	1239	0.14
EO33	95	1.99	9131	0.602



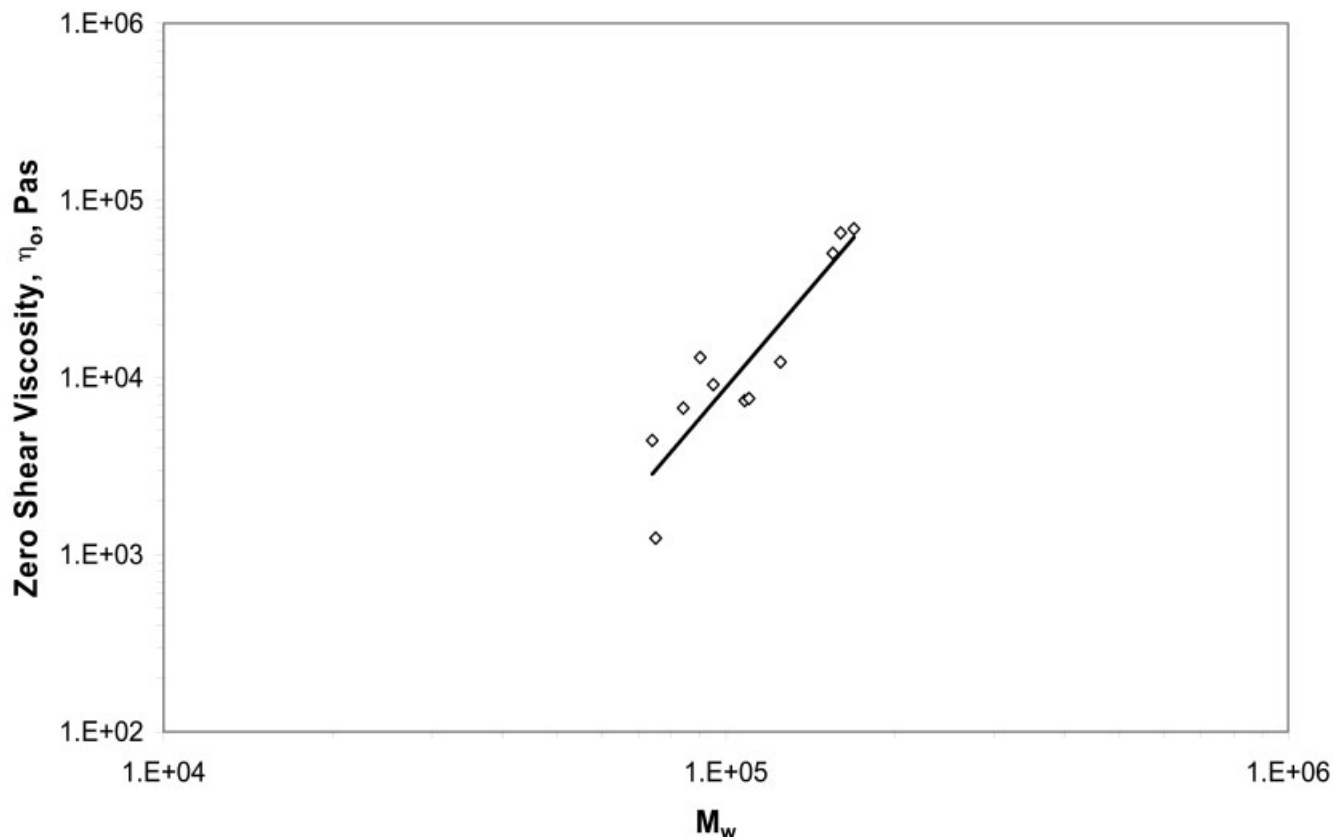


Figure 8  $\eta_0(M_w)$  for linear and branched PEs ( $T_{\text{test}} = 190^\circ\text{C}$ ;  $\gamma^0 = 15\%$ ).

different m-PEs with different BC were somewhat scattered. The whole set of data was correlated by  $\eta_0 = K(M_w)^\alpha$  with  $K = 2 \times 10^{-15}$  (Pa s/[g/mol]<sup>3.7</sup>) and  $\alpha = 3.7$ . The calculated value of the exponent is close to that reported for linear PEs.<sup>3,8</sup>

#### Flow activation energy (E): influence of molecular parameters

When  $\log \eta^*$  is plotted against  $1/T$  over wide ranges of temperature ( $T > T_g + 100$ ), even for liquids of low  $M_w$ , the apparent value of  $E$  decreased as  $T$  increased,<sup>30</sup> since viscosity is sensitive to the extra free volume created by thermal expansion.<sup>31</sup> For non-Newtonian materials, viscosity at fixed temperature is dependent on shear stress ( $\tau$ ) or shear rate ( $\dot{\gamma}$ ), hence either  $A$  or  $E$  or both must be considered as functions of  $\tau$  or  $\dot{\gamma}$ . The modified flow activation energy,  $E_\tau$  or  $E_{\dot{\gamma}}$  were given by  $R[\delta \ln \eta / \delta(1/T)]_\tau$  or  $R[\delta \ln \eta / \delta(1/T)]_{\dot{\gamma}}$ <sup>32</sup> with  $E_\tau \cong E_{\dot{\gamma}} \cong E$  at low shear rate (i.e. in the Newtonian limit). However, disagreement exists in the literature on the effect of  $\tau$  on  $E$ . While some reported an increase in  $E$  with  $\tau$ ,<sup>33</sup> others observed a decrease<sup>34</sup> or no influence of shear stress on flow activation energy.<sup>35</sup>

Here, temperature sweep tests were performed on all resins at constant frequency and strain. The objec-

tive of these tests was to evaluate the flow activation energy ( $E$ ) of the different resins and correlate  $E$  to molecular structure. The test was conducted in the range 160–260°C with a temperature ramp of 5°C/min at  $\omega = 1$  rad/s and  $\gamma^0 = 15\%$ . The values of  $E$  were calculated for all PEs by fitting complex viscosity data to Arrhenius relation ( $\eta^* = A e^{E/RT}$ , where  $A$  is a constant). Results are presented in Table III.

Figure 9 shows a plot of  $E$  versus  $M_w$ . Flow activation energy is found to decrease with increasing  $M_w$ .

TABLE III  
Flow Activation Energies

Sample ID	$M_w$ (kg/mol)	MWD	BC CH <sub>3</sub> /1000 C	$E$ (kcal/mol)
LM1	160	2.35	0	4.56
LM2	169	2.17	0	3.89
LM3	155	2.07	0	–
EB15	108	1.95	14.5	6.01
EB19	110	1.78	18.5	6.40
EB42	125	1.81	42	5.95
EO15	84	1.47	15.9	7.61
EO16	90	2.04	16.3	6.96
EO19	74	2.10	18.7	7.82
EO26	75	1.40	25.9	9.27
EO33	95	1.99	32.7	7.54

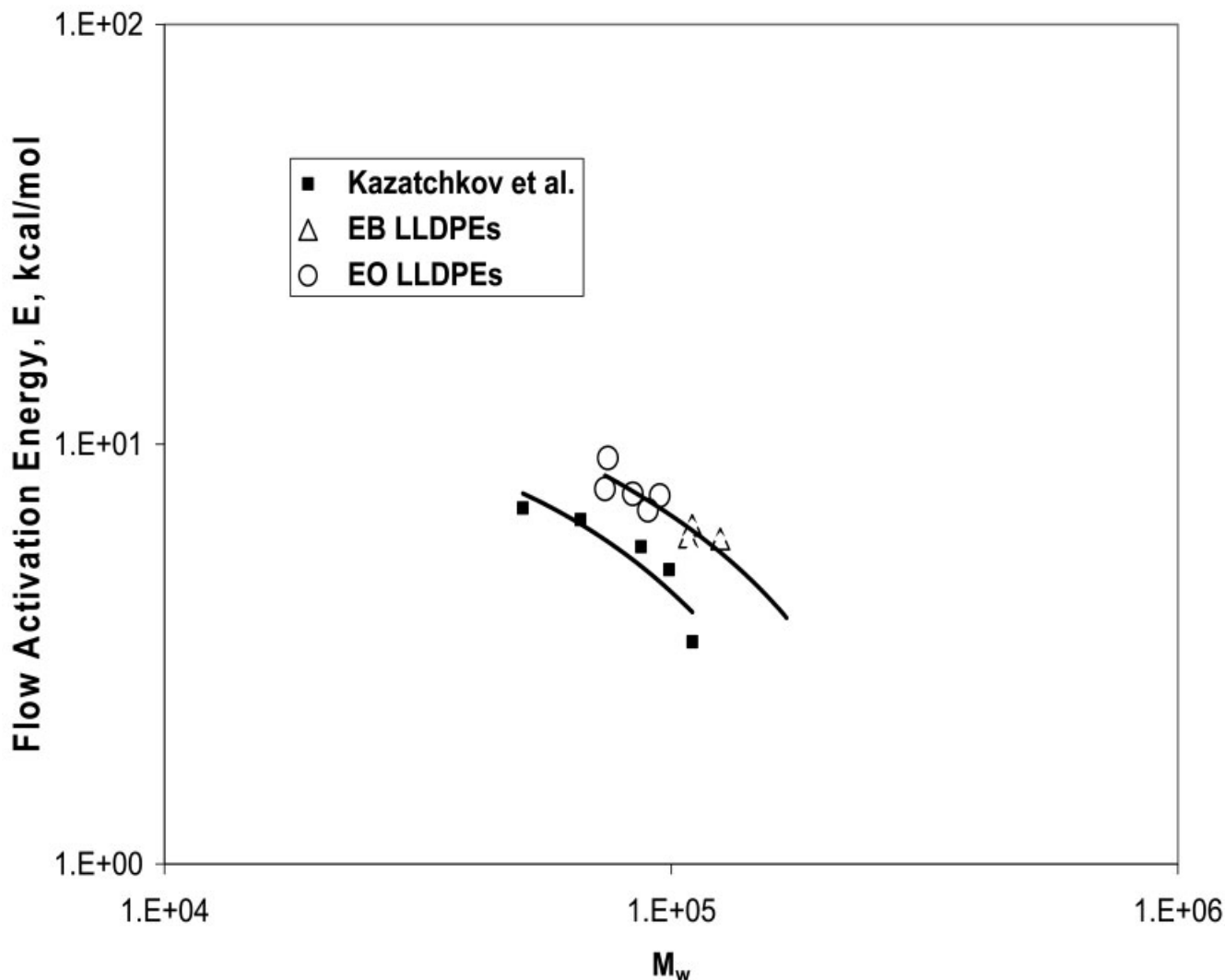


Figure 9  $E(M_w)$  for linear and branched PEs ( $T_{\text{test}} = 160\text{--}260^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

Kazatchkov et al.<sup>4</sup> reported a decrease in flow activation energy with an increase in  $M_w$ , whereas it increased with the increase in polydispersity of the resin. We have plotted the values given in reference<sup>4</sup> together with our data in Figure 9. The trend of our data and that of Kazatchkov et al. are very similar although our values are relatively higher. In general, the values reported in reference<sup>4</sup> are lower than those of other researchers.<sup>8,14</sup>

Finally, Figure 10 shows the influence of BC on the flow activation energy. Two sets of m-LLDPEs containing butene and octene copolymers were chosen such that BC was the only dominant variable. The flow activation energy for ethylene–octene copolymers is observed to be always higher than their butene counterparts LLDPEs. These results are in agreement with previous reports.<sup>14</sup> This increase in activation energy has been associated with the increase in molar volume of the repeating unit of the polymer.<sup>27</sup> It is also worth noting that values of  $E$

for m-LLDPEs are always higher than linear PEs (see Table III). Vega et al.<sup>8</sup> evaluated the flow activation energies for a large number of linear and hexene–ethylene copolymers with a wide range of  $M_w$  (63–327 kg/mol) and SCB (2.34–48.5 CH<sub>3</sub>/1000C). Their plot of  $E$  versus branch content showed a scattered data. However, they were able to derive a relation  $E = 5.7 + 6.4[1 - \exp(-\text{SCB}/35.4)]$  to fit the data well for linear and short chain branched polyethylene samples. It was also mentioned that the relation was not suitable for bimodal commercial polymers having low  $M_w$  tails or polymers suspected of containing long chain branching. When we compared our data to the model proposed by Vega et al.,<sup>8</sup> we did see an agreement in the trend although the values did not match. We suspect that this disagreement could be due to two reasons. First, no influence of  $M_w$  was taken into account in their model, although the  $M_w$  for their polymers ranged from 63 to 327 kg/mol and  $M_w$  does influence  $E$  as

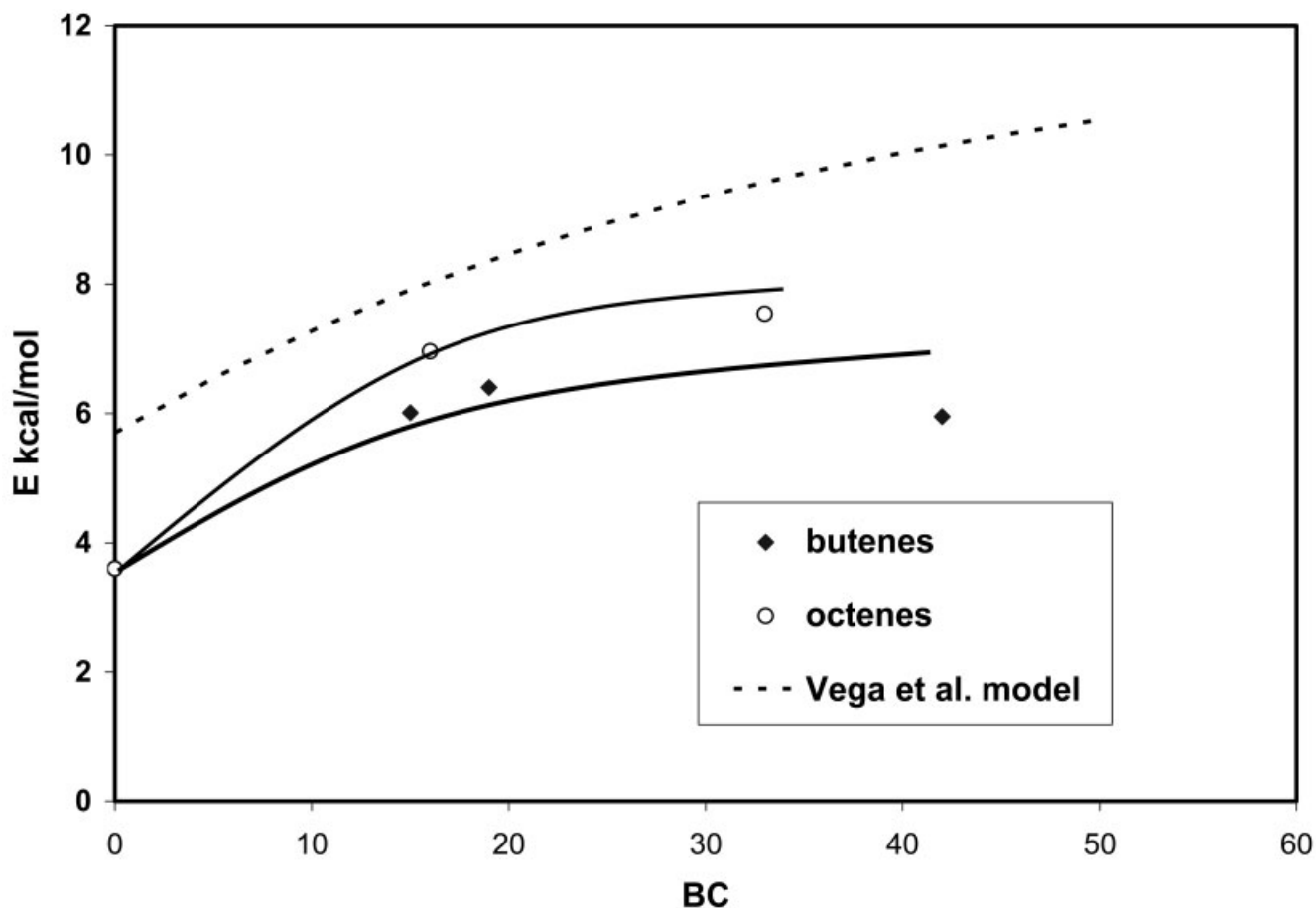


Figure 10 E(BC) for linear and branched PEs ( $T_{\text{test}} = 160\text{--}260^\circ\text{C}$ ;  $\gamma^\circ = 15\%$ ).

discussed earlier. Second, we suspect that difference of comonomer type could be another important factor considering the aforementioned results (Fig. 5). Resins used by Vega et al. were linear PEs and hexene–ethylene copolymers, whereas polymers used in this study are butene and octene copolymers.

### CONCLUSIONS

Linear rheology of linear HDPE and m-LLDPEs was successfully investigated. Molecular parameters such as  $M_w$ , branch type, and MWD were found to influence viscoelastic behavior of both m-PEs. The increase in  $M_w$  has increased the viscosity at low- $\omega$ , whereas BC had little effect on viscoelastic properties. It was found that comonomer type also affects the viscoelastic behavior. Plots of  $\log G'$  versus  $\log G''$  were very helpful in revealing the influence of comonomer type on the viscoelastic behavior of PEs. For resins of similar comonomer type grouped together, flow activation energy was found to be influenced by both  $M_w$  and BC. Different trends were observed for octene and butene LLDPEs with respect to flow activation energy,

with ethylene–octene LLDPEs showing higher values of  $E$  than their butene counterparts.

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