

A Rheological Study of Long Branching in Polyethylene by Blending

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Synopsis

Steady shear viscosities, dynamic viscosities and moduli, and the corresponding activation energies for flow were examined for a branched polyethylene, a linear polyethylene, and three of their blends at 150° and 190°C. The polyethylenes were chosen to have closely matched molecular weights and distributions. An R-17 Weissenberg rheogoniometer and an Instron capillary rheometer were used. At lower stress, the branched polymer had a higher viscosity than the linear one, possibly because of the contribution of long branches to entanglements. At high stress, this contribution is reduced and the inherently smaller coil dimensions likely become responsible for the lower viscosity of the branched polymer. The activation energy for the branched polymer is high and decreases with stress, in contrast to the low and almost-constant value for the linear polymer. The effects here of pressure on compression are considered. The entanglements of long branches may also decrease with increasing temperature. With decreasing stress, the activation energy for branched polymer tends to become constant, corresponding to an absence of pressure effects and an equilibrium entanglement of long branches for a given temperature range. The linear relationship between activation energy and blend composition probably means that any compressional effects, like free volume, are additive and that long-branch entanglements rearrange with added linear molecules. The linearity may be the result, in part, of a broad distribution for the lengths of long branches.

INTRODUCTION

The rheological characteristics of branched (low-density) polyethylene have been previously contrasted with the corresponding properties of linear (high-density) polyethylene. Prominent distinctions are evident in plots of η_0 -versus- M_w , E^* -versus- M_w , and E^* -versus- τ relationships, as well as in the absolute value of E^* ,¹⁻⁸ where τ is shear stress, η_0 is low-shear Newtonian viscosity, and M_w is weight-average molecular weight. For low-density polyethylene, η_0 depends on M_w to a power much greater than the usual 3.4 ± 0.1 for linear amorphous polymers. The temperature coefficient of viscosity, as expressed in terms of activation energy E^* , also depends on M_w at high molecular weights and exceeds the limit found for linear polyethylene.^{2,3} Among the distinctive features for low-density polyethylene probably the most interesting is the unusually high E^* , up to 18 kcal/mole, and its marked decrease with τ .^{1,4,5}

For another polymer, poly(vinyl acetate), a study has shown that a composition with long branches also had a higher E^* than the corresponding linear polymer. The higher values were here reduced toward the lower E^* of a linear poly(vinyl acetate) on addition of sufficient low molecular weight diluent.⁹ Such a phenomenon was explained by a breakdown of long-branch entanglements suggested to be responsible for the higher activation energies.

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Long branches in polyethylene are also postulated to be responsible for the anomalous flow behavior and activation energy.¹ However, the possible mechanism for the influence of long-chain branches has not been established. A larger size of the flow unit due to long branches, in the Eyring sense, is one rationale.

It seemed, therefore, of interest to study the effect of dilution of a branched polyethylene by a linear polyethylene. Namely, a study seems worthwhile of the controlled elimination of branch entanglements induced by dilution with a linear polyethylene and to note the effect on η_0 , E^* , and their dependence on shear.

Rheological studies were made on two characterized polyethylenes that differed widely in branching and on three of their blends. As branching in polyethylene is generally associated with a broadening of molecular weight distribution, which also effects certain rheological behavior, the two polyethylenes were selected to have approximately the same molecular weight and molecular weight distribution. As a convenient consequence, the two polyethylenes and their blends thus had similar viscosities so that the same instrumentation could be used to explore a broad range of long-chain branching compositions.

The limiting values of E^* at low shear were explored using a Weissenberg rheogoniometer. The high stress range was investigated using an Instron capillary rheometer. In addition, the dynamic viscoelastic properties of the polyethylenes and blends were studied with the Weissenberg rheogoniometer R-17.

EXPERIMENTAL

Materials

The branched and linear polyethylenes selected for the study were obtained from Arco Polymers, Monroeville, Pennsylvania. The branched polymer had a melt index (conditions E) of 0.24 g/10 min and a density of 0.918 g/ml at 23°C. The values for the linear material were 0.5 g/10 min and 0.965 g/ml, respectively.

The blends of these two polyethylenes were prepared by means of a Kenics mixer having a diameter of 0.375 in. and a length of 2 in. The mixer was placed in the barrel of an Instron capillary rheometer just above a capillary with a length of 1.0 in. and a diameter of 0.03 in. The mixture of pellets of the two polyethylenes was fed in the barrel heated at 190°C and extruded at a rate of approximately 4 ml/min. The extrudate was then cut in pieces about $\frac{1}{8}$ in. long and well mixed. This procedure was repeated four times for each blend. In addition to the molecular weights and branching analysis of the blends, the efficiency of blending was also initially demonstrated by blending individual components with and without dispersed carbon black.

Three blends were prepared having branched polyethylene weight fraction of 0.25, 0.50, and 0.75. These values are used in this paper to designate the blends. Consequently, the samples 0.0 and 1.0 correspond to undiluted linear and branched polyethylenes, respectively.

Branching Analysis

The five samples were analyzed for short and intermediate branches and for long branches. All measurements are expressed as number of branches per 1000 CH₂ units. The definitions of the lengths of the branches are based on the analytic capabilities: all chain ends are counted by infrared absorption analysis (methyl groups at 7.75 μm, ethyl at 12.95 μm, and vinyl at 11.00 μm), and the number of long-chain branches is calculated from dilute solution viscosity and gel permeation data since branching lowers the limiting viscosity number. The methods cited in references 10–12 have been used for data treatment. Thus, by reducing the number of all chain ends per 1000 CH₂ units by $(2.0 \times 1000)/(M_n/14)$ (to account for the assumption that each macromolecule of $M_n/14$ CH₂ units contains two chain ends which are not counted as branches) and then reducing this result by the number of long branches, one obtains the total number of short (ethyl groups) and intermediate branches.

Gel permeation analyses were carried out in *o*-dichlorobenzene at 135°C using a Model 200 gel permeation chromatograph manufactured by Waters Associates, Inc.

Rheological Characterization

Three types of tests were made on each of the five samples, viz the branched and linear polyethylenes and their three blends. Two temperatures, 150° and 190°C, were used for the Instron steady-shear tests which were performed using a 0.05 × 2.0 in. tungsten carbide capillary of 90° entrance angle at 11 shear rates from 0.289 to 578 sec⁻¹. The experiments with a Weissenberg rheogoniometer Model 17 were made with a 1.0-in.-diameter plate and a cone of the same dimension and a 4° cone angle. In the Weissenberg steady shear experiments, the torque and the normal force were measured at nine shear rates from 0.0017 to 1.7 sec⁻¹. In the Weissenberg oscillatory shear tests, the amplitude ratio of strain and stress waves and the phase angle between them were measured by means of a Tronotec phasemeter Model 702A at seven frequencies: 9.48, 3.0, 0.948, 0.3, 0.948, 0.03, and 0.00948 cycles/sec and at a strain amplitude not exceeding 0.02 radian.

RESULTS AND DISCUSSION

The results of molecular weights, limiting viscosity number, and branching measurements are given in Table I. Considering the limiting viscosity number and the number of short and intermediate branches, one concludes that the values for the blends are as expected from values for original branched and linear polyethylenes and blends composition. The same is true, within the limits of precision, for number-average molecular weight. This would prove correct composition and blending procedure. But weight- and number-average molecular weights and, more specifically, the number of long branches found for blends are lower than expected. This suggests a modest degradation of macromolecules during the blending procedure and/or a limitation in the precision of the GPC method. Namely, such a decrease in long branching must lead to measurably lower molecular weights, even if only branched macromolecules were degraded, which is not observed by either GPC and limiting viscosity number

TABLE I
Molecular Weights, Limiting Viscosity Number, and Branching of Branched and Linear Polyethylenes and Their Blends

Branched polyethylene (Dylan 1000 F WPD 4784)	Blend composition, wt-%				
	100	75	50	25	0
Linear polyethylene (Super Dylan 7004)	0	25	50	75	100
Molecular weights by GPC (branching corrected)					
\bar{M}_n	16,000	13,000	15,000	11,000	11,000
Calculated for blends, \bar{M}_n		14,390	13,060	11,950	
\bar{M}_w	166,000	154,000	138,000	139,000	172,000
\bar{M}_z	1,811,000	1,290,000	1,058,000	1,006,000	1,535,000
Limiting viscosity number, dl/g (<i>o</i> -dichlorobenzene, 135°C)	1.020	1.128	1.270	1.438	1.618
Calculated for blends		1.170	1.319	1.469	
Short and intermediate branches per 1000 CH ₂	27.9	21.2	15.0	7.5	0.7
Calculated for blends		21.1	14.3	7.5	
Long branches per 1000 CH ₂	0.90	0.53	0.19	0.06	0.05
Calculated for blends		0.69	0.48	0.26	

techniques. In other words, the GPC data on M_n and on long branching exhibit a disparity.

The Instron capillary rheometer data were plotted as shear stress versus shear rate (uncorrected) to evaluate parameters and to perform the Rabinowitch correction. The corrected values are herewith reported. The torque and normal forces measured in the Weissenberg steady shear tests provided τ , η_a (apparent viscosity), and $P_{11} - P_{22}$ (first normal stress difference). The amplitude ratio and phase angle yielded the values for G' , G'' , η' , and η^* , which are the real and imaginary components of the complex dynamic shear modulus and the real and complex dynamic viscosity, respectively.

Figure 1 shows the internal consistency of Instron and Weissenberg steady shear viscosities, as well as the good superposition of this curve with the plot of complex dynamic viscosity versus angular frequency for the linear polyethylene, the branched polyethylene, and the 50–50 blend of the two polyethylenes. A similar conclusion has been drawn by Onogi.⁸ The slightly lower values of the Weissenberg steady shear viscosity at high shear in certain cases may be due to a minor loss of polymers from the Weissenberg gap.

Figures 2 and 3 show the regular trend of viscosity as a function of composition at a series of constant capillary shear stresses for 190° and 150°C, respectively. Evident are the similarity of viscosities for the two blended polymers, the regular transition between the two with varying composition, and the greater shear and temperature sensitivity of the branched polymer. Significantly, entanglements of long branches must be contributing to the low shear viscosities since the branched polyethylene exhibits higher viscosities in this region yet has a lower M_w than the linear polyethylene. A comparison of Figures 2 and 3 indicates a change in temperature dependence with composition. A conventional temperature reduction of data for all samples will thus not be applicable.

Figures 4 and 5 are plots of viscosity versus shear stress for the linear and branched polyethylene and their three blends, as obtained by the Instron cap-

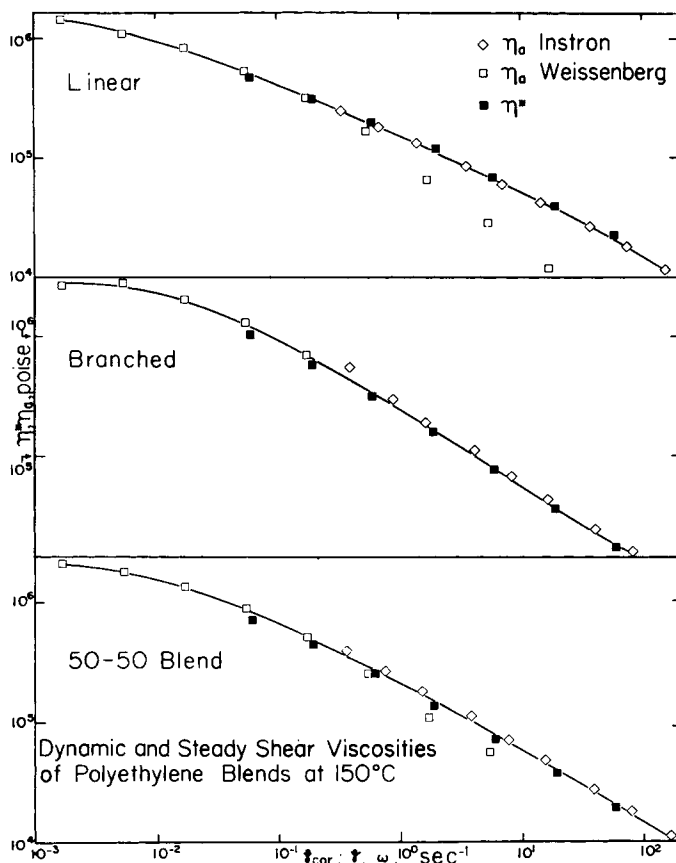


Fig. 1. Viscosity vs corrected shear rate obtained by Instron capillary rheometer, viscosity vs shear rate by Weissenberg rheogoniometer, and complex dynamic viscosity vs angular frequency for linear polyethylene (sample 0.0), branched polyethylene (sample 1.0), and their blend (sample 0.50) at 150°C. (\diamond) η_a Instron; (\square) η_a Weissenberg; (\blacksquare) η^* .

illary rheometer at 150° and 190°C. It may be noted that the linear and branched polyethylenes have matched viscosities at an intermediate stress near 10^6 and 6×10^5 dynes/cm² at 150° and 190°C, respectively. The viscosity of the branched polymer decreases with stress more rapidly than does the linear polyethylene. This is likely due to a marked reduction in the contribution of long branches to molecular entanglements since the MWD for the branched polyethylene is actually narrower than for the linear. Namely, the entanglements involving long branches plausibly and apparently add a stress sensitivity beyond that for main-chain entanglements. Thus, for approximately the same M_w , the branched polymer has a higher viscosity at lower stress because of the contribution of long branches to entanglements. At higher stress and at higher temperature, this contribution is reduced. The effects of branching expressed in Figures 4 and 5 is consistent with prior results on polyethylene¹⁴ and on polybutadiene.¹⁵

The plots of apparent viscosity η_a versus stress (resulting from both Instron and Weissenberg steady shear tests) were used to calculate the flow activation energy at constant stress,

$$E_\tau = R \times 2.303 \times (\log \eta_{150} - \log \eta_{190}) / (1/423 - 1/463)$$

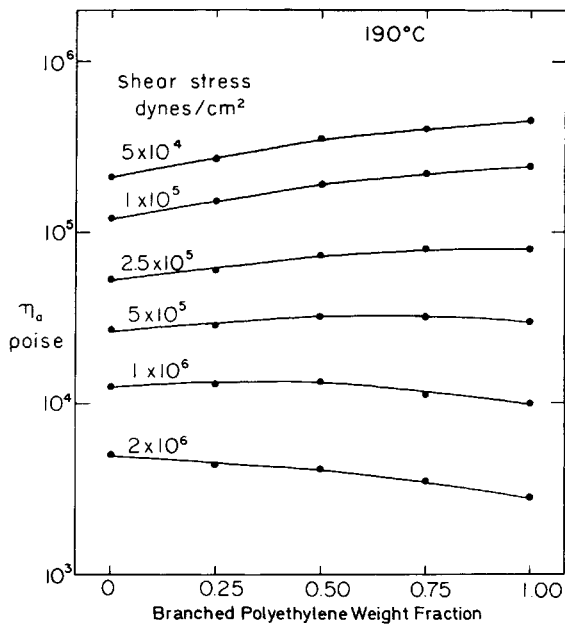


Fig. 2. Instron rheometer data on two polyethylenes and their blends. Viscosity vs branched polyethylene weight fraction at 190°C at a series of constant shear stresses.

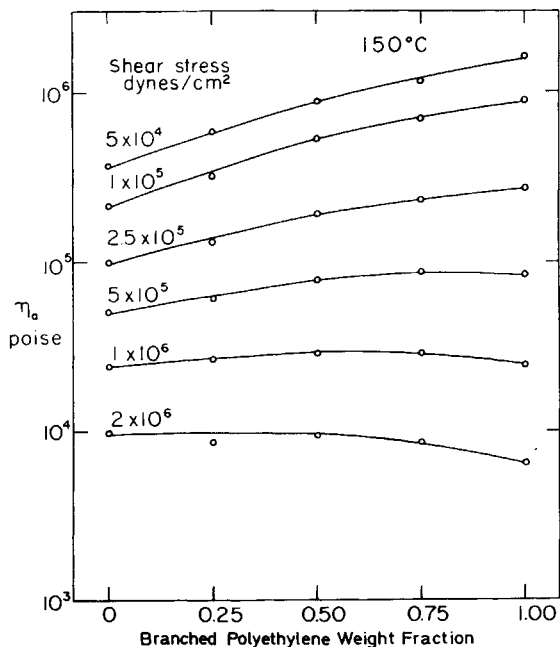


Fig. 3. Instron rheometer data on two polyethylenes and their blends. Viscosity vs branched polyethylene weight fraction at 150°C at a series of constant shear stresses.

which are given in Table II. In Figure 6 these results are plotted as E_τ versus τ . The much higher value of E_τ for branched polyethylene and its decrease with stress may be compared to the virtually constant value for linear polyethylene. This effect may also be due to entanglements of long branches. It is likely that

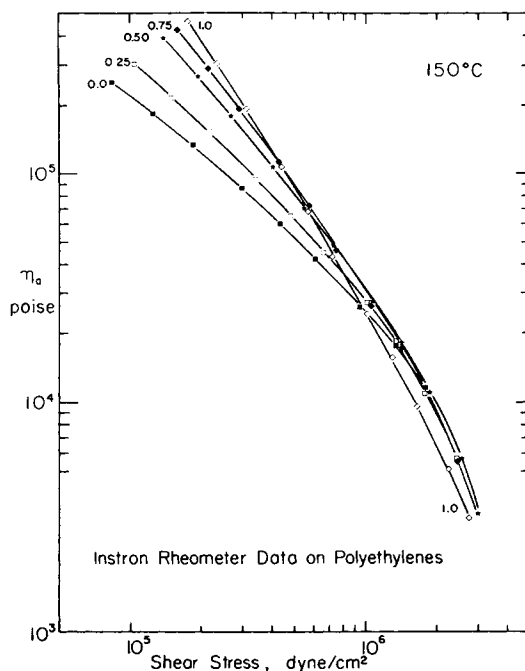


Fig. 4. Viscosity vs shear stress obtained by the Instron capillary rheometer for samples at 150°C.

the entanglements of long branches influence not only the coil dimensions and coordination of molecular movements, as evident from melt viscosity enhancement, but also the flow unit size. With increasing stress, main-chain and branch entanglements are reduced as manifested in a viscosity decrease. Long-branch disentanglements are apparently more sensitive to changes in shear, i.e., the lowering of E_τ with τ . Considering E_τ as a temperature coefficient of viscosity, long-branch entanglements can also be supposed to be more temperature sensitive than main-chain entanglements. With decreasing stress, E_τ tends to become constant. This may correspond to an equilibrium state for long-branch entanglements for the temperatures involved. Prior Instron rheometer data, only at higher stresses, have not shown this leveling out of E_τ at lower stress.^{1,5}

In Figure 7, E_τ^* is plotted as a function of blend composition. This correlation is linear within the precision of measurements. This suggests that the fractional contribution of long-branch entanglements to the average flow unit size is proportional to concentration as branched molecules are diluted by linear chains. This corresponds to a complete compatibility and ability of linear molecules to disentangle and "solvate" the branched molecules. It is thus likely that en-

TABLE II
Activation Energy of Complex Dynamic Viscosity of Linear and Branched Polyethylenes
Between 150° and 190°C

Polyethylene	$\eta^* \times \omega$, dynes/cm ²				
	5×10^4	1×10^5	2.5×10^5	5×10^5	1×10^6
Linear		5.0	5.5	5.6	5.7
Branched	13.7	12.9	11.2	10.0	8.2

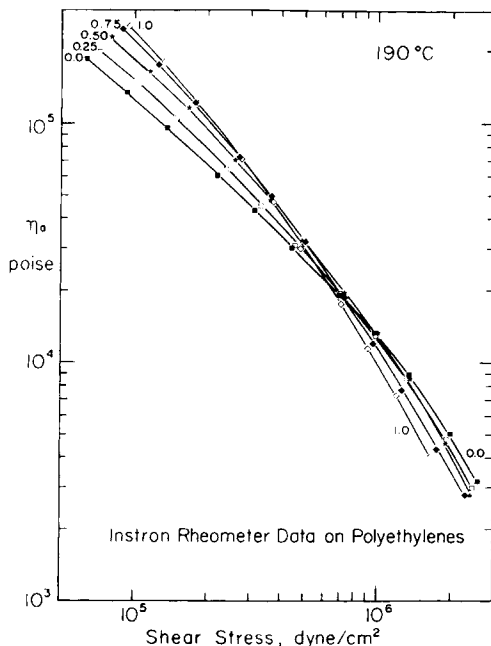


Fig. 5. Viscosity vs shear stress obtained by the Instron capillary rheometer for samples at 190°C.

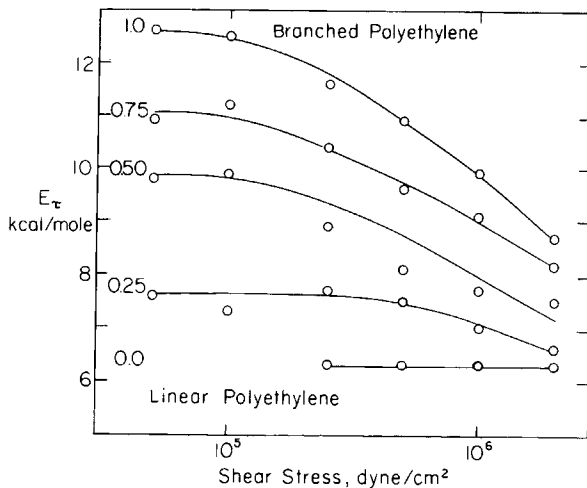


Fig. 6. Activation energy for steady shear viscosity at constant stress vs stress, between 150° and 190°C.

tanglements of long branches are rearranged among linear molecules to give again almost the same contribution to the average flow unit size. This could be further elucidated by studying the dilution of branched polyethylene with progressively lower molecular weight linear polyethylenes, down to those below the chain length critical for entanglements, viz., a molecular weight near 4000.¹³ The featureless dependence in Figure 7 may also be due to the nature of the long branches. They may represent, in polyethylene, a very broad range in the lengths of long branches. It may even be probable that in branched polymers of more defined

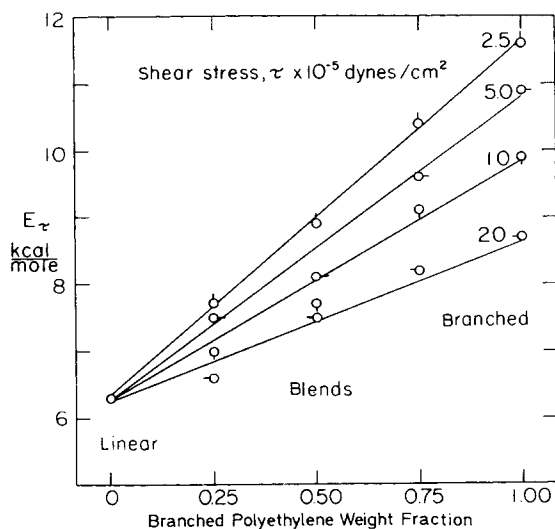


Fig. 7. Activation energy for steady shear viscosity at constant stress vs blend composition (branched component weight fraction), between 150° and 190°C at four indicated stress values.

geometries, one will be able, in essence, to develop a rheometric titration of long branches.

The dynamic results provide some interesting features, as seen from Table II. The plots of η^* versus $\eta^* \times \omega$ were used to calculate an activation energy for complex dynamic viscosity. Here again, the values for linear polyethylene are much lower and constant as compared to the values for branched polyethylene, which also clearly decrease with increasing dynamic stress, defined as the product $\eta^* \times \omega$. An interesting point here is that activation energy decreases, yet there is no pressure effect and a shear contribution to disentanglement is unlikely.

Figure 8 shows that the first normal stress difference at 150°C increases with the fraction of branched polyethylene in the blends. As a manifestation of melt elasticity, this can be expected on the basis of a long-branch contribution to incremental entanglements. At 190°C the entanglements of long branches are apparently reduced, as indicated by viscosity and activation energy changes.

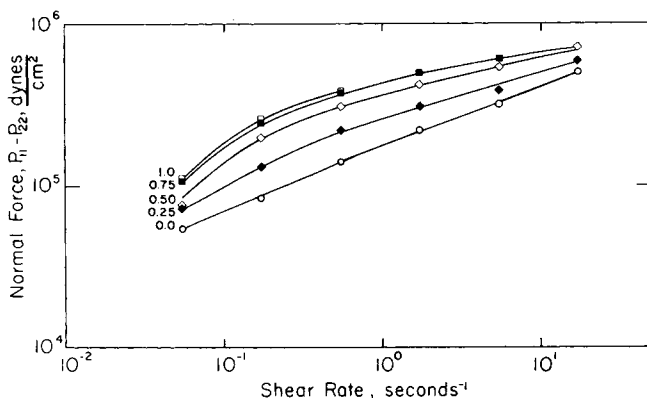


Fig. 8. Normal stress difference from Weissenberg steady shear experiments vs shear rate for five indicated samples, at 150°C: (O) linear polyethylene (sample 0.0); (□) branched polyethylene (sample 1.0); other symbols, blends as indicated.

Consistently, their contribution to the first normal stress difference is also reduced at 190°C (see Fig. 9).

The storage modulus, another expression of polymer melt elasticity, increases also with branched polyethylene content (see data at 190° and 150°C in Figs. 9 and 10, respectively). The convergence of all curves at higher angular frequencies must reflect the interaction of shorter segments less influenced by entanglements and long branches. At 190°C the behavior of both unblended polyethylenes is almost the same, even at low frequency, consistent with less entanglement of long branches at higher temperature. The changes in first normal stress difference and in G' can be considered in terms of blending of linear molecules, with differences from these predictions being possible effects of long-chain branching. Since the molecular weights and distributions of the polymers are similar, very small, if any, changes in normal force and in G' are

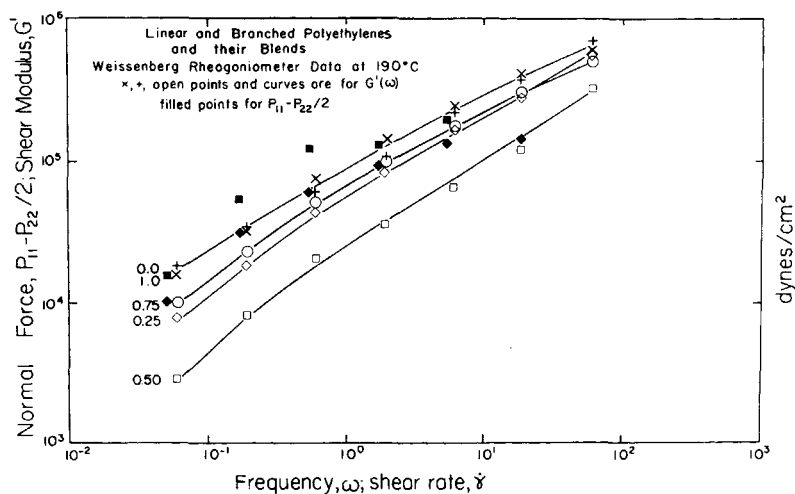


Fig. 9. Storage shear modulus vs angular frequency and normal force vs shear rate for five indicated samples (linear and branched polyethylenes and their blends) at 190°C.

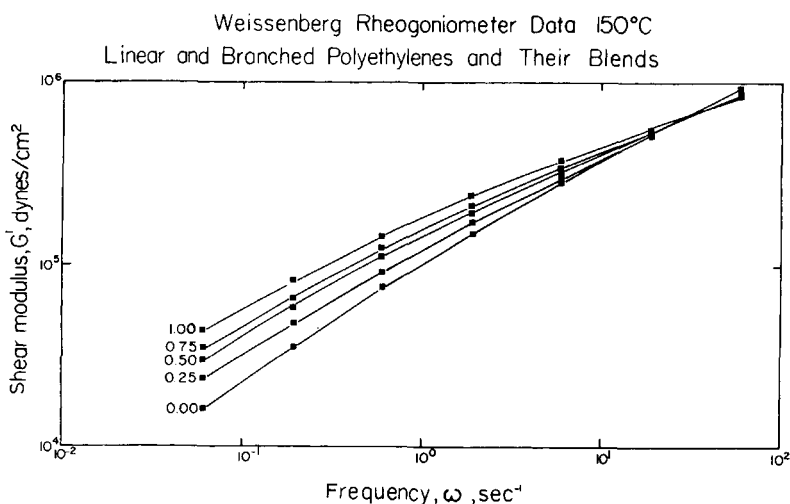


Fig. 10. Storage shear modulus vs angular frequency for five indicated samples (linear and branched polyethylenes and their blends). Weissenberg rheogoniometer data, at 150°C.

expected for their blends.⁷ Indeed, it was found that G' and $P_{11} - P_{22}$ for the blends were generally similar to those for the two starting polyethylenes.

Moreover, as expected, the starting branched and linear polyethylenes had similar values even at low ω and $\dot{\gamma}$, with values becoming indistinguishable for starting polymers and blends as ω and $\dot{\gamma}$ were increased from near the terminal region up to the approach to the plateau region. Figure 9 indicates (1) verification of the expression $G' = (P_{11} - P_{22})/2$ at equivalent ω and $\dot{\gamma}$ and that (2) the long-chain branching in the starting polymer and in the blends with linear polyethylene produced no dramatic effects in these values. At 190°C, Figure 9 shows that the two starting polyethylenes have G' -versus- ω spectra which are matched within experimental error. Representative normal force data are also given at the equivalent shear rate. At 150°C, Figure 10 shows that the two polymers are distinctly different with the moduli (and normal forces) for the blends generally being intermediate. This indicates a measurable difference in the temperature dependence for these viscoelastic functions as well as in the more widely studied property of steady shear viscosity. Here at 150°C, as well as 190°C, $G'_{(\omega)} \approx (P_{11} - P_{22})/2$. The match was excellent at intermediate values near 1 sec^{-1} , but at lower values G' was lower, and at higher rates G' was generally higher. The spectrum apparently being observed for these polyethylenes and blends is a long region of monotonic changes with time and frequency. The theoretical limits of slope are being approached but were not actually observed. These would be 2.0 and near 0 for the terminal and plateau regions, respectively,⁷ for Figures 9 and 10.

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