

# Time-Temperature Superposition - A Users Guide

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## Abstract

Time-temperature superposition is a valuable tool for describing the viscoelastic behavior of linear polymers over a broad range of times or frequencies by shifting data obtained at several temperatures to a common reference temperature. This technique involves the use of temperature-dependent shift factors for the magnitudes of measured stresses (vertical shift factor) and for time or frequency (horizontal shift factor) on log-log plots of material functions such as the relaxation modulus, the storage and loss moduli, and the creep compliance. The temperature-dependent, vertical shift factor  $b_T$  is usually defined so that it multiplies a stress determined at temperature  $T$  to yield a "reduced stress" that is the value at a "reference temperature,"  $T_0$ ; it is normally very close to unity. The temperature-dependent horizontal shift factor  $a_T$  multiplies a frequency or divides a time to yield a reduced value equal to  $a_T\omega$  or  $t/a_T$ . If time-temperature superposition is obeyed, the use of shift factors will yield a "master curve" showing viscoelastic behavior over a much larger range of times or frequencies than could be studied using a single rheometer at one temperature. However, a shift factor valid in the plateau and terminal zones is not expected to be applicable in the transition zone. And the success of superposition should not be judged on the basis of a small log-log plot or imprecise data.

## Introduction

A single rheometer operated at a single temperature can usually provide data only over a range of three or four decades of frequency or time, and this is inadequate to track viscoelastic behavior from the high-frequency end of the plateau zone into the low-frequency terminal zone. By obtaining data at several temperatures, time-temperature superposition can be used to generate a "master curve" showing the behavior at a "reference temperature" that covers many decades of time or frequency. A material to which this technique is applicable is said to be "thermorheologically simple."

In preparing master curves, variables having units of time (or reciprocal time) are subject to horizontal shift, while those having units of stress (or reciprocal stress) are subject to vertical shift. For example, in preparing a compliance "master curve," the variable plotted on the vertical axis is  $J(t)/b_T$ , and that plotted on the horizontal axis is  $t/a_T$  where both  $a_T$  and  $b_T$  are shift factors that depend on temperature.

Thermorheological simplicity obtains when all contributing retardation or relaxation mechanisms of the material have the same temperature dependence and when stress magnitudes at all times or frequencies have the same temperature dependence. This implies that when viscoelastic functions, such as the relaxation modulus  $G(t)$  or the creep compliance  $J(t)$ , are shown on a double-logarithmic plot, data at various temperatures can be shifted horizontally by a constant (independent of time) distance identified as  $\log(a_T)$  and vertically by another constant distance identified as  $b_T$  to obtain a single master curve bringing together all the data. The master curve displays data over a wide range of frequencies or times "reduced" to a reference temperature,  $T_0$ . A thorough discussion of time-temperature superposition can be found in the book by Ferry [1, Section 11-C], who also discusses the shifting of data obtained at several pressures.

We can summarize the above discussion by saying that a master curve of the frequency-dependent storage modulus, based on data obtained at various temperatures  $T$  is obtained by plotting:

$$b_T G'(T) \text{ versus } \omega a_T \quad (1)$$

using logarithmic scales for both axes. While it is not indicated explicitly,  $b_T$  and  $a_T$  are functions of temperature, although the  $b_T$  dependence is quite weak.

The quantity on the left is called the "reduced storage modulus," sometimes given the symbol  $G'_r$ , while the reduced frequency is  $\omega_r$ . Using these variables, the master curve is a plot of  $G'_r$  versus  $\omega_r$ . And the temperature dependence is usually reported by means of a plot of  $\log(a_T)$  versus  $T$ .

Likewise, for the time-dependent stress relaxation modulus a master curve is obtained by plotting

$$b_T G(T) \text{ versus } t/a_T \quad (2)$$

again using logarithmic scales. This can be written in terms of reduced variables as  $G_r$  versus  $t_r$ . However, the reader should be aware that an alternative definition of  $b_T$  has been used, particularly in the earlier publications of Graessley and his colleagues and in the recent book by

Rubinstein and Colby [2]. In these publications the reduced modulus is  $(1/b_T)G(t)$ .

The concept of time-temperature superposition can be expressed in terms of an equation relating the property at the reference temperature  $T_0$  to that measured at a temperature  $T$  and then shifted to  $T_0$ :

$$b_T G'(T, \omega a_T) = G'(T_0, \omega) \quad (3)$$

or:

$$G'_r(T, \omega_r) = G'(T_0, \omega)$$

However, some authors write the equality in a different way, which can cause confusion.

Viscosity, which involves both stress and time, requires the application of both shift factors. For example, a master curve of the absolute value of the complex viscosity is constructed by means of a double-logarithmic plot of

$$\frac{b_T}{a_T} |\eta^*|(T) \quad \text{versus} \quad \omega a_T \quad (4)$$

where

$$|\eta^*| = \sqrt{G'^2 + G''^2} / \omega$$

A special case is the zero-shear viscosity.

$$\frac{b_T(T)}{a_T(T)} \eta_0(T) = \eta_0(T_0) \quad (5)$$

If the vertical shift factor is taken to be unity, the horizontal shift factor can be inferred from the zero-shear viscosity.

$$a_T(T) = \frac{\eta_0(T)}{\eta_0(T_0)}$$

Since viscosity is then proportional to the shift factor, the viscosity ratio or even the viscosity itself  $\eta_0(T)$  is often used as a horizontal shift factor.

One can determine the horizontal shift factor without making any assumption about  $b_T(T)$  by plotting as a function of frequency a quantity that is not affected by  $b_T$ , such as the loss angle or its tangent, which is equal to  $G''/G'$ .

Controlled strain rheometers are best suited for measurements at moderate and high frequencies, while controlled torque (stress) instruments are more useful at lower frequencies. However, it often happens that neither oscillatory shear method can provide data in the terminal zone, and creep and creep recovery are used to provide the missing information. The combination of data from these two techniques to produce a single master curve requires a method for conversion of one material function, for example the creep compliance, into another, for example the storage modulus. One approach to this conversion was proposed by He *et al.* [3]. It is important to note that while creep recovery is the most accurate method for determining the steady-state compliance, often called the steady-state recoverable compliance for this reason, is a challenge. In air-bearing instruments, residual torque prevents the reduction of the stress to zero. Either this must be corrected for using a model or a magnetic suspension used in place of an air bearing.

In the case of crystallizable melts, the useful temperature range extends only from the crystallization temperature, on the low end, to the degradation temperature, at the high end, and this limits the applicability of superposition to these polymers.

The compilation of data obtained at several temperatures inevitably adds noise into the resulting master curve. And this noise can interfere with the use of a master curve to determine the molecular weight distribution [4] by the differentiation of  $|\eta^*|$  with respect to frequency.

## Theoretical basis for time-temperature superposition

### Vertical shift factor

The Bueche-Rouse theories of the linear viscoelasticity of unentangled polymer melts and solutions [5,6] assumes that stress magnitudes, *e.g.*,  $G(t)$ ,  $G'(\omega)$  and  $G''(\omega)$ , are proportional to the product of the density and temperature. This implies that the vertical shift factor  $b_T(T)$  is:

$$b_T = T_0 \rho_0 / T \rho \quad (6)$$

For entangled polymer systems, the molecular models most widely used are based on the theory of Doi and Edwards [7], which predicts that the magnitude of the relaxation modulus of an entangled melt is proportional to the factor  $\rho T$  that appears in the Rouse prediction multiplied by a new factor that depends very weakly on temperature. Thus the vertical shift factor is predicted to be slightly different from the  $\rho T$  ratio, but data are rarely if ever precise enough to reveal this difference.

Rather than using Eq. 6, the vertical shift factor is sometimes determined directly from the variation with temperature of a distinctive value of the modulus or

compliance, such as a maximum or minimum in the loss modulus. The plateau in the relaxation modulus  $G(t)$ , the creep compliance  $J(t)$ , the storage modulus  $G'(\omega)$  or the storage compliance  $J'(\omega)$  is also sometimes used. However, since true plateaus with zero slopes are not actually observed, the values at the associated maxima or minima provide more reliable bases for  $b_T(T)$ . Although its precise measurement poses challenges, the steady-state compliance provides a reliable basis for finding  $b_T(T)$ , as demonstrated by Resch *et al.* [8] and Plazek [9]. Another way to determine the vertical (stress) shift factor that is independent of the time or frequency shift is to find the horizontal shift of loss angle data required to obtain superposition on a plot of loss angle versus  $\log |G''|$ , which is called a Van Gurp-Palmen plot [10].

The vertical shift factor is sometimes used as a fitting parameter for an entire set of data, and the data are shifted both vertically and horizontally in an attempt to achieve a superposition that “looks OK”. This empirical procedure can help to disguise the failure of superposition by averaging the discrepancy over the entire frequency range. Systematic deviations of  $b_T(T)$  from its expected behavior (Eq. 6) can also result from experimental errors. Finally, if both shifts are carried out by fitting, neither factor has any physical significance. For these reasons, such results are questionable.

#### Horizontal shift factor

What do molecular models tell us about the horizontal shift factor? The relaxation times of the Rouse model and those appearing in tube models for the plateau and terminal zones, all depend on temperature in the same way; they are proportional to the ratio  $\zeta/T$ , where  $\zeta$  is the monomeric friction coefficient. If the friction coefficient does not depend on stress or deformation, and if its dependence  $T$  were known *a priori*, a single shift factor would be applicable from the early portion of the transition zone dominated by Rouse relaxations into the terminal zone, and  $a_T(T)$  could be calculated from theory. However, this observation does not allow the prediction of the shift factor, because the monomeric friction coefficient is an empirical parameter in the freely-jointed chain model, and its value can only be inferred from rheological data. Thus, while all the theories mentioned above predict thermorheological simplicity over the time or frequency range of their applicability, in the plateau and terminal zones, they do not lead to a prediction of  $a_T(T)$ .

It is important to note that the Rouse-Bueche model for unentangled polymers and tube models for entangled molecules are based on the freely-jointed chain model, in which the actual molecule is replaced by a much simpler structure that makes it possible to make

quantitative predictions of viscoelastic behavior. This picture has been found to work very well in describing behavior in the plateau and terminal zones and in the longest-time (lowest-frequency) portion of the transition zone. But at shorter times, relaxation modes involving parts of molecules smaller than the segments of the freely-jointed chain come into play, and these are not described by the models discussed above. As a result, a value of  $a_T$  obtained using data in the terminal and plateau zones will not serve to superpose data obtained at significantly shorter times (higher frequencies). Plazek and his coworkers [11-13] have reported exceptionally precise and accurate creep data over many decades of time for several amorphous polymers and have used these to demonstrate the failure of time-temperature superposition (occurrence of thermorheological complexity) when one tries to place all the data on a single master curve using a single value of  $a_T$  at a given temperature. Sometimes, reasonable superposition can be obtained over very wide time/frequency ranges by using two or more horizontal shift factors [14,15] for different time/frequency zones. For polydisperse samples, there is a gradual transition from one zone to another, so one must examine the data carefully to detect the beginnings of thermorheological complexity as the frequency is increased. It is also important to note that short-time relaxation mechanisms will come into play at longer times as the temperature is lowered. One must therefore be on the alert for complexity not only at short times (high frequencies) but also at low temperatures.

Since  $a_T$  cannot be predicted, horizontal shifting is carried out by shifting data until they appear to superpose. Honerkamp and Weese [16] have described a procedure for doing this in an objective manner, and software for this procedure is part of the IRIS package [17].

How does  $a_T$  depend on temperature? Early observations of the dependence of liquid viscosity on temperature led to the empirical Arrhenius relationship that can be expressed in terms of  $a_T$  as follows:

$$a_T(T) = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (7)$$

And this relationship has been found to fit data for linear polymers in the plateau and terminal zones as long as the temperature is well above  $T_g$ . By analogy with reaction rate theory, the constant  $E_a$  has come to be called the activation energy for flow. However, the activation energy concept is often used to characterize polymers even when rheological data do not superpose, and this results in ambiguity as to the meaning of  $E_a$ . For

example,  $E_a$  is sometimes reported to vary with frequency or time or modulus. Various approaches have been proposed for identifying a meaningful activation energy when data do not superpose. One example is a value based on  $\eta_0$ . Several ways of defining  $E_a$  values in the absence of superposition have been compared by Wood-Adams and Costeux [18], and Keßner *et al.* [19] have recently discussed this issue in detail. It is clear that in reporting activation energies for flow, it is essential to explain in detail how these were determined. And one must not compare values obtained in different ways. In any event, when data do not superpose, the use of an activation energy to characterize a polymer is somewhat questionable.

For temperatures closer to  $T_g$ , the fractional or relative free volume concept of Doolittle provided the basis for the WLF (Williams, Landel, Ferry) equation (Eq. 8), a complete discussion of which can be found in Ferry [1, Sections 11-B,C].

$$\log a_T = \frac{-c_1(T-T_0)}{[c_2 + (T-T_0)]} \quad (8)$$

where  $c_1$  and  $c_2$  are empirical constants.

### Judging the success of superposition

The degree to which superposition is successful is rarely judged on the basis of an objective criterion. And one should not rely on software to make this judgment. Most often one simply looks at the shifted data and declares that time-temperature was successful or unsuccessful. This is particularly true for a portion of a curve that has a slope much less than one, where a significant failure of horizontal superposition results in a shifted data point that is close to the trend line but is actually far from where it should be. Wood-Adams and Costeux [18] proposed the use of linear rather than logarithmic scales to detect complexity. Figure 1 shows data for a metallocene polyethylene homopolymer with a very low level of long-chain branching. On this log-log plot the data appear to superpose well, but the linear plot shown in Figure 2 shows clearly that this material is not thermorheologically simple. In this example, the detection of complexity

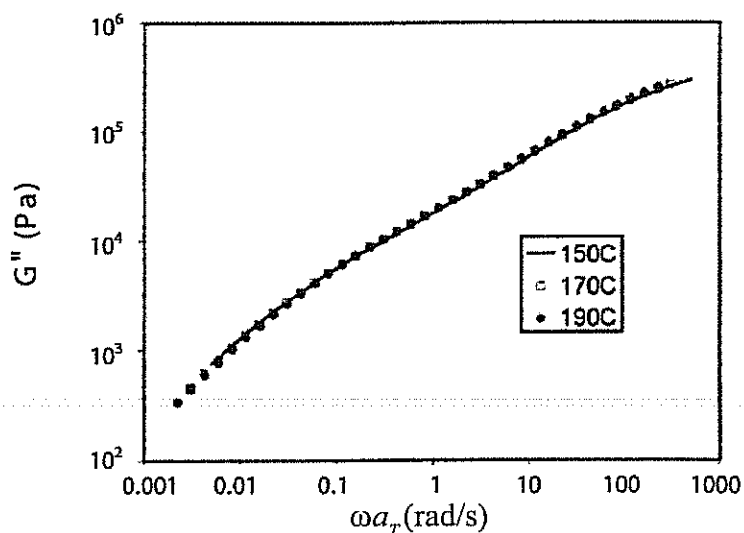


Figure 1: Master curve of loss modulus of a lightly-branched metallocene polyethylene [18]. Logarithmic scales are used for both axes. Note that the vertical shift factor is taken to be unity.

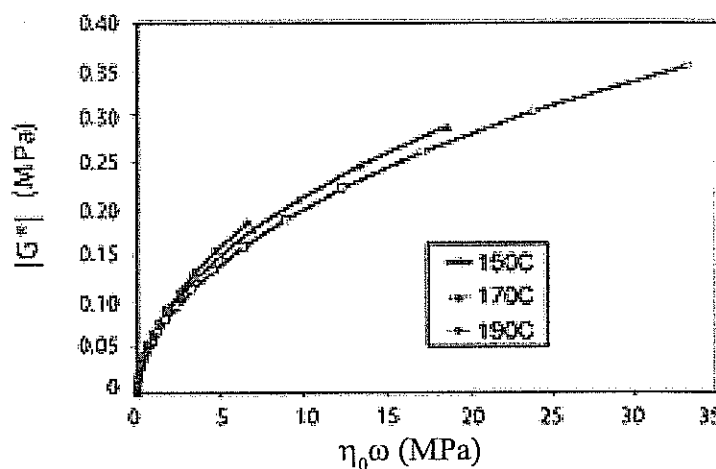


Figure 2: Master curve of absolute value of the complex modulus of the polymer of Fig. 1 [18]. Linear scales are used for both axes. The vertical shift factor is taken to be unity, and the zero-shear viscosity is used as the horizontal shift factor.

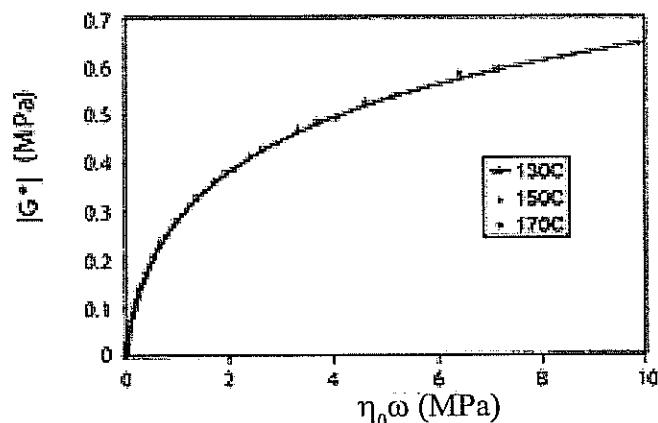


Figure 3: Master curve of absolute value of the complex modulus of a linear polyethylene/octene copolymer [18]. Linear scales are used for both axes. The vertical shift factor is taken to be unity, and the zero-shear viscosity is used as the horizontal shift factor.

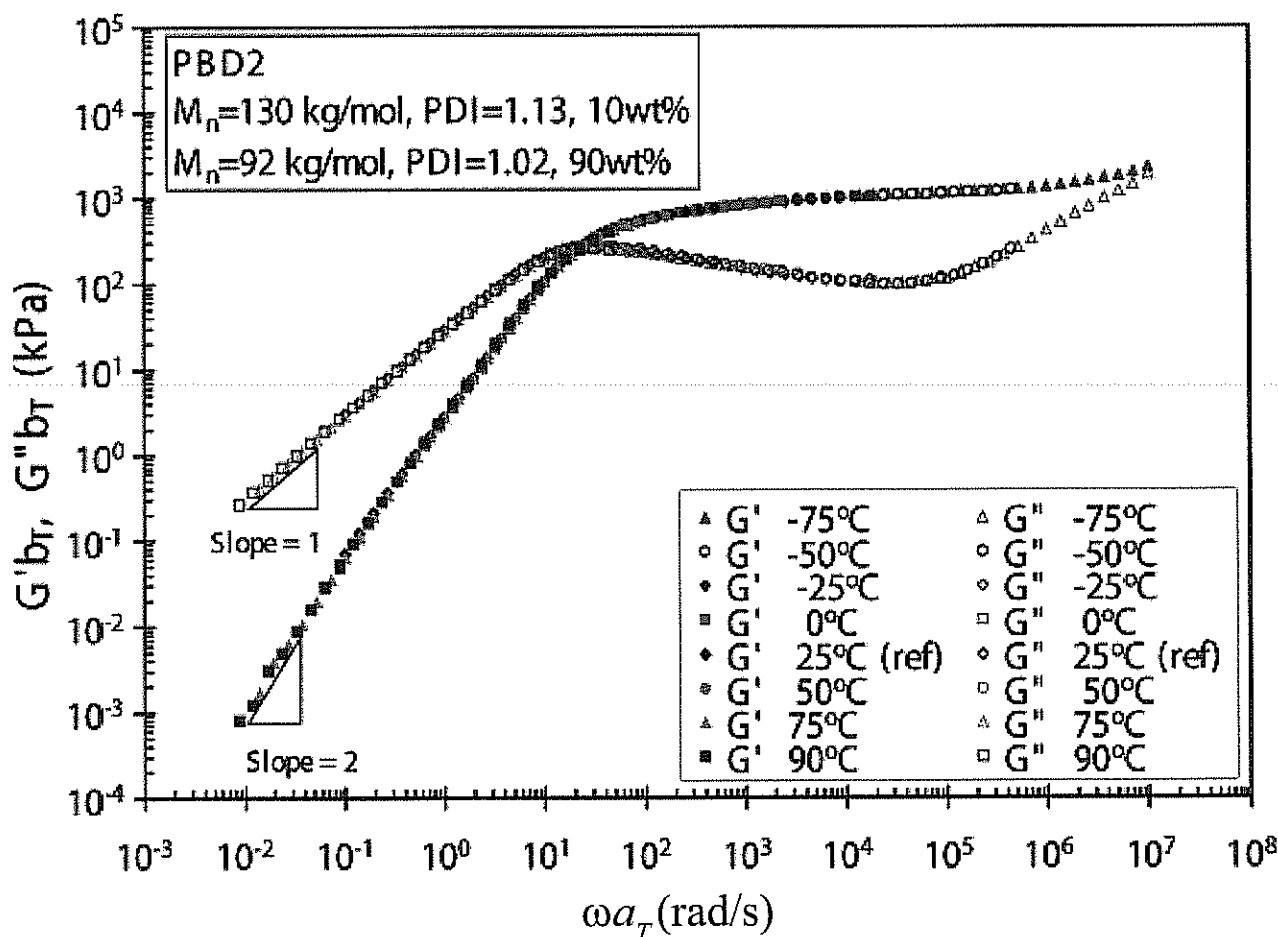


Figure 4: Master curves of storage and loss moduli of a polybutadiene blend based on data obtained at eight temperatures. These data superpose well. (Data of Michelle Li and Hee Eon Park measured at McGill University)

is important, as it provides evidence of long-chain branching. Figure 3 shows the master curve using linear scales for a linear ethylene/butene copolymer that exhibits excellent superposability. Note that the zero-shear viscosity has been used as the horizontal shift factor, while the vertical shift factor is taken to be unity. Sometimes it is claimed that data superposed, but no plot is shown; such a statement must be considered doubtful.

A simple and direct technique for detecting complexity is the use of a van Gurp-Palmen plot [10] of loss angle versus  $\log|G^*|$ . If the effect of  $b_T$  on the magnitude of the complex modulus is negligible, the data will superpose without shifting if the material is thermorheologically simple.

The degree of thermorheological complexity may not have serious consequences if only a general trend is of

interest, but when one wishes to infer structural features from data, it becomes very important. For a highly-entangled polymer, molecular structure is revealed by behavior in the plateau and terminal zones, and data in the transition zone and at even shorter times are not of interest for this application. In fact, rheological behavior is more sensitive to the presence of small quantities of large molecules than chromatography.

#### How well does it work?

Figure 4 is master curve of data obtained at eight temperatures for a blend of two linear polybutadienes. Each point is an average of three measurements, and the vertical shift factor was calculated using Eq. 6. Careful inspection reveals a few small deviations from superposition but, taking into account the precision obtainable in this type of measurement, the superposition is deemed to be acceptable.

(continues page 30)

A material will exhibit thermorheological simplicity if all of its relaxation times have the same dependence on temperature. As demonstrated above, we expect this to be so in the plateau and terminal zones. And this should continue to be the case as we move into the transition zone, as long as relaxation is governed by Rouse modes. However, it is not possible to say in advance over what portion of the transition zone data will superpose. Molecular models based the freely-jointed chain picture must fail for processes involving portions of the chain smaller than the imaginary "subunit" that makes up this chain. And another complication at high frequencies (short times) is that as the entropy spring modes are damped, the glassy modes of relaxation become dominant [20]. We expect then that shift factors based on data in the plateau and terminal zones will always fail at some point not far beyond (higher frequencies or shorter times) the plateau zone.

### Nonlinear properties

Graessley [21, p. 239] provides a discussion of the application of time-temperature superposition to nonlinear properties, and we provide here only a brief summary. The viscosity function has been reported to obey time-temperature superposition. If the vertical shift factor is neglected, the zero-shear viscosity can be used as the horizontal shift factor to obtain a master curve by plotting

$$\frac{\eta(T, \dot{\gamma})}{\eta_0(T)} \text{ versus } \eta_0(T) \dot{\gamma} \quad (9)$$

The other viscometric functions can also be treated in this manner. But viscometric functions are not functions of time; what about time-dependent properties? Constitutive equations for melts almost universally build on the same spectra of relaxation times that are used to describe linear viscoelasticity. This implies that if time-temperature superposition brings linear data together, it should also work for nonlinear properties using the same shift factors. The fundamental assumption is that the relaxation times are independent of the state of stress. For example, a temperature-invariant representation of the shear stress-growth coefficient is based on the following relationship:

$$\frac{b_T}{a_T} \eta^+(t/a_T, \dot{\gamma} a_T, T) = \eta^+(t, \dot{\gamma}, T_0) \quad (10)$$

Muller and Froelich [22] applied time-temperature superposition to extensional stress-growth data.

### Structural features contributing to complexity

The most successful demonstrations of superposition have involved linear homopolymers, and complexity is often observed in the case of more complex molecules. Variations in the local microstructure of linear polybutadienes resulting from hydrogenation to various extents were found not to result in deviations from simplicity [23], and all the polymers produced in that study were found to have the same horizontal shift factor when the reference temperature was  $T_g + 50^\circ\text{C}$ . As we might have expected, these shift factors did not superpose data obtained at frequencies well above the plateau region [24] because of the prominence of segmental relaxations in this region.

Wood-Adams and Costeux [18] found that the very short branches in ethylene-octene copolymers did not result in thermorheological complexity. The effect of long-chain branching depends on a combination of chain chemistry and molecular architecture. Metallocene polyethylenes containing low levels of long-chain branching have been found to be thermorheologically complex [18, 25]. Polyisoprene stars have the same shift factors as the linear polymer [26]. Kapnistos *et al.* [27] studied a series of polybutadienes having star-like backbones with grafted branches and reported that the shift factors were the same for all the structures that they used. Moreover, these were the same as shift factors reported previously for linear and comb polybutadienes. On the other hand, data for hydrogenated polybutadiene stars were not superposable [28], although their unhydrogenated precursors exhibited simple behavior [29]. This anomalous behavior has been examined by Graessley [30] and a theoretical explanation has been proposed [31].

Low-density polyethylene has a complex structure that involves both long and short branches, and it is known to be thermorheologically complex.

### Acknowledgements

The authors benefited from lengthy discussions with W. W. Graessley, and comments on a draft of the manuscript from Ute Keßner of the University of Erlangen. However, it is not to be inferred that these individuals are in agreement with every statement made in the paper. Michelle Li and Hee Eon Park worked for several weeks to obtain the data shown in Fig. 4 and provided the plot. Jen Shueng Tiang read the "final" manuscript very carefully and found many ways to improve it.

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