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Time–Temperature Superposition and Linear Viscoelasticity of Polybutadienes

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ABSTRACT: A series of monodisperse polybutadienes has been used to perform mechanical relaxation measurements from the flow regime to the glassy state. Results on loss shear moduli have been analyzed within the framework of a coupling model. It has been found to represent well the frequency dependence in the glassy and terminal zones using a segmental motion coupling parameter β_α and an entanglement coupling parameter β_η. Moreover, our results on apparent shift factors resulting from time–temperature superposition are consistent with the lack of thermorheological simplicity predicted by the coupling theory due to the difference between β_α and β_η.

Introduction

In recent years there has been considerable interest in the study of the dynamics of glass-forming systems and particularly in glass-forming polymeric systems. In this latter case it has been claimed that the relaxation behavior around the calorimetric glass–rubber transition temperature T_g (or α-relaxation) is different from the relaxation behavior associated with the rubber–liquid transition (or terminal zone) far above T_g.[1] It is widely believed that the α-relaxation is associated with segmental motion of local parts of the polymer chain, whereas the terminal behavior is associated with translational motion of the whole chain according to the reptation concept of de Gennes.[2] Many techniques including mechanical, dielectric, NMR relaxations, and quasi-elastic light scattering allow one to obtain complex susceptibilities in one or both zones. A non-Debye frequency behavior is always observed. In the case of high molecular weight polymers, the two relaxation processes mentioned above are well separated and the loss modulus measured shows two distinct peaks. In most cases, each of these peaks is well represented using a stretched-exponential relaxation function:

$$\Phi(t) \propto \exp(-(t/\lambda)^\beta) \tag{1}$$

known as the Kohlrausch–Williams–Watts (KWW) function (see ref 3 for a review).

It should be noted that this type of curve fitting is mainly used for the α-relaxation. In connection with Ngai's coupling model, this equation has been used also for the terminal relaxation.[4] However, in the terminal zone it is often preferred to use a sum of weighted exponentials as a fitting function in connection with normal-mode theories of the molecular motion[5,6] which predict a spectrum of relaxation times. The KWW function implies a spectrum of relaxation times[7] whose breadth is connected with the parameter β.

It is well-known that each technique used to obtain relaxation data at a given temperature has a limited time or frequency window that seldom covers the entire range of interest. It has become a common practice to shift isothermal viscoelastic or dielectric data by the same amount (shift factor a_T) along the log frequency or log time axis in order to obtain master curves extending over a wider range than the original data.

Shift factors are defined as:

$$a_T = \lambda(T)/\lambda(T_r) \tag{2}$$

where λ is obtained from eq 1 (or an equivalent fitting procedure) and T_r is the reference temperature.

This empirical procedure is known as the time–temperature superposition principle or thermorheological simplicity.[8] It is well documented for melts from the terminal zone to the rubbery zone. In this case, its validity is attributed to the fact that each relaxation process is equally affected by the temperature, and thus the shape of the relaxation process is temperature invariant. When dealing with temperature behavior below T_g to well above T_g and with a large experimental window in the time or frequency domain, thermorheological simplicity should be checked, invoking two types of considerations. First, the parameters β_α (glassy or softening zone) and β_η (terminal zone) should be temperature independent. Second, the relative position of the α-relaxation zone and of the terminal zone in the time domain should not vary with temperature, and thus the relaxation times of each peak (e.g., λ_α and λ_η) should have the same temperature dependence.

Concerning the first requirement for thermorheological simplicity, it is largely admitted that it is fulfilled for the relaxation time spectrum of homopolymer melts in the terminal relaxation zone.[8] However, in the softening zone near T_g, this point is still a matter of discussion.

On the basis of dielectric measurements on low molecular weight polymers, it has been found that β_α is temperature dependent.[9] A similar result has been found by Cavaillé et al.,[10] based on the measurement of the complex shear modulus of a low molecular weight polystyrene.

For high molecular weight polymers the actual picture is more confusing. Various isothermal dielectric loss curves obtained by Boese and Kremer[11] on polyisoprene melts can be fitted using a unique value of 0.4 for β_α. Instead, the dielectric loss curves obtained by Zetsche et al.[12] on a poly(vinyl methyl ether) (PVME) showed a shape independent of the temperature in the range $\{T_g + 4\ °C, T_g + 50\ °C\}$ whereas Colmenero et al.[13] obtained

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a strong temperature dependence of β_α for high molecular weight poly(vinylethylene) (PVE) in the range $\{T_g - 10\ °C, T_g + 50\ °C\}$.

It should be noted, however, that even when the time–temperature superposition principle is not strictly valid according to the first criteria, it is always possible to define shift factors as:

$$a_T = \omega_{\max}(T)/\omega_{\max}(T_r) \tag{3}$$

were $\omega_{\max}$ is the frequency at the loss peak and T_r the reference temperature.

Concerning the second requirement, Plazek was the first to mention that the temperature dependences of the softening and terminal dispersions are different (see Plazek[14] and Ngai[15] for a review). It should be noted that a direct comparison between the shift factor obtained for the α-process $(a_T)_\alpha$ and for the terminal zone $(a_T)_\eta$ requires techniques with a very large time window such as broad-band dielectric devices or special mechanical rheometers. For instance, results of Plazek have been obtained using isothermal creep measurements extending over 6 decades in time. Boese and Kremer[11] using dielectric spectroscopy extending over 10 decades in frequency were able to determine simultaneously $(a_T)_\alpha$ and $(a_T)_\eta$ in the range $\{T_g + 20\ °C, T_g + 130\ °C\}$ for low and high molecular weight polyisoprene. They stated that $(a_T)_\eta$ shows a weaker temperature dependence than $(a_T)_\alpha$ although the difference was very weak in this range of temperatures. With the same technique Ngai et al.[16] obtained, on low molecular weight poly(propylene glycol), results analogous to Plazek's.

Ngai and coworkers[1,17] were able to interpret these differences in temperature behavior within the framework of a coupling theory.[7,17] According to this approach, the nonexponential character of the relaxation (e.g., eq 1) is related to the cooperative interactions occurring between polymer chains. If the chain, in absence of coupling, relaxes in an exponential fashion with a characteristic primitive time λ_0, the effective relaxation time λ is related to λ_0 by:

$$\lambda \propto \lambda_0^{1/\beta} \tag{4}$$

As the degree of cooperativity of the Rouse modes decreases with increasing the rank of the mode, it is assumed that the relaxation is mostly due to the modified first mode.

Furthermore, the molecular processes are different in the softening and terminal zones. Thus, the related coupling parameters β_α and β_η are different, although the friction factor of the underlying primitive relaxation time λ_0 is the same. The two corresponding shift factors are then related by the relation:

$$\beta_\eta \log (a_T)_\eta = \beta_\alpha \log (a_T)_\alpha = \log (a_T)_0 \tag{5}$$

where $(a_T)_0$ is the underlying shift factor corresponding to the λ_0 temperature dependence.

It should be pointed out that eqs 1 and 5 imply that the frequency and temperature behavior are correlated.

Finally, in the terminal zone the model predicts for high molecular weight linear polymers a power law dependence of the zero-shear rate viscosity η_0 upon the molecular weight M:

$$\eta_0 \propto M^{2/\beta_\eta} \tag{6}$$

As most linear polymers show a 3.4 exponent, this leads to a coupling parameter β_η of about 0.59, independent of the polymer.

Table 1. Physico-chemical Characterization of the Polybutadienes Studied

	M_n[a]	M_w[b]	M_w/M_n[b]	T_g[c] (°C)
TV514	50 000	51 260	1.12	−86.9
TV510	70 000	70 600	1.16	−86.5
LV498	87 000	85 800	1.12	−86.2
TV506	210 000	228 500	1.16	−86
TV504	320 000	464 400	1.14	−85

[a] Osmometry values furnished by Michelin. [b] GPC measurement by Université du Mans. [c] DSC.

The theory was particularly successful[1] in correlating the thermorheological simplicity of a polyisobutylene with the fact that creep measurements indicated almost the same value for the two coupling parameters β_η and β_α. In contrast, polystyrenes with narrow molecular weight distributions showed no thermorheological simplicity and different values of coupling parameters.[14,17]

The aim of this paper is to investigate the validity of the time–temperature superposition principle for a series of polybutadienes with the same microstructure. We have determined their dynamic moduli using classical mechanical measurements in a range of temperatures extending well above and below T_g. The results will be interpreted within the framework of the coupling model which is actually the only theory taking into account the above-mentioned experimental results. Because many previous results have been obtained for commercial polymer melts or low molecular weight ones, we will concentrate in this study on nearly monodisperse polybutadienes with molecular weights well above the molecular weight between entanglements, M_e.

Experimental Section

Materials. A homogeneous series consisting of five polybutadiene homopolymers, obtained by anionic polymerization, was supplied by Michelin (France) and has been used for this study. All the samples present the same chain microstructure, i.e., 11% of 1,2-vinyl and 48% of 1,4-trans sequences.

Molecular determinations have been carried out at room temperature in tetrahydrofuran with a classical analytical SEC apparatus coupled to a multiangle light scattering recently developed in the University du Maine (France).[18] The light scattering average molecular weights (M_w) and molecular weight distribution values (M_w/M_n) are reported in Table 1 as well as sample references used in this work.

The glass transition temperature (T_g) was determined by differential scanning calorimetry. Measurements were made at a heating rate of 10 °C/min. Results are given in Table 1. A slight dependence of T_g upon molecular mass is observed.

Carella et al.[19] have shown that, for polybutadienes, the glass transition temperature is a function of the vinyl content, and the mean value of −86 °C obtained for our series of polybutadiene with the same microstructure correlates well with their results.

Rheological Measurements. Melt viscoelastic studies were carried out in a dynamic regime using a Rheometrics RMS 800 rheometer in order to obtain isothermal dynamic moduli data $G'(\omega)$ and $G''(\omega)$. The experimental frequencies ranged from 10^{-1} to 100 rad/s for each temperature. The range of temperatures was −115 to +80 °C. Temperature regulation was done using N_2 gas in order to avoid any structural modification. In all cases we have ensured the linearity of the stress response with respect to the strain amplitude in order to remain within the linear viscoelastic domain. A cone and plate configuration was used from +80 to −75 °C. At lower temperatures this configuration is no longer suitable due to a slip of the sample, and instead we used a torsional rectangular sample configuration.

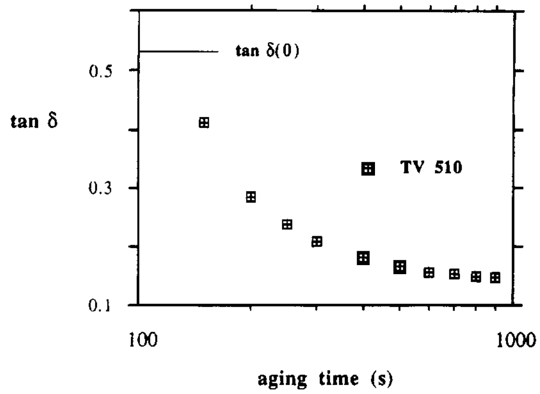

Figure 1. tan δ ($=G''/G'$) versus the aging time, at 1 rad/s for the sample TV510 quenched from T_g to $T_g - 10$ °C.

Table 2. Rheological Data of the Polybutadienes Studied

	η_0 (25 °C) (Pa·s)	$J_e^0 \times 10^6$ (Pa)	$G_N^0 \times 10^{-6}$ (Pa)
TV504	8.1×10^6	2.2	1.7
TV506	1.1×10^6	2.8	1.8
LV498	4.2×10^4	2	2.15
TV510	1.7×10^4	2.1	2
TV514	4.1×10^3	1.9	1.55

Finally, for temperatures below the glass transition another problem is encountered due to structural recovery during isothermal annealing under T_g. This phenomenon known as physical aging will influence dynamical properties (for a recent review, see McKenna[20]). Figure 1 shows the evolution of tan δ ($=G''/G'$) at 1 rad/s with the aging time after a quench from T_g to $T_g - 10$ °C for one of the polybutadienes used in this work. The final temperature is reached within 200 s, but an apparent mechanical steady state seems to be reached in almost 1000 s. Obviously kinetics are influenced by the amplitude of the temperature step, and a time to recover a steady state as long as 10^6 s was observed for a 20 °C step below T_g on poly(methyl methacrylate).[21]

In order to minimize this effect, we used the same procedure for all our measurements.

Samples were shaped at −50 °C and then placed in the measurement cell at the same temperature. Isothermal measurements between 10^{-1} and 10^2 rad/s were then carried out on the same sample with a decrement of 5 °C between each temperature of measurement. For each temperature step we have observed an equilibrium time of 1000 s at rest before starting the cycle of measurements which lasts about 1000 s. Thus, the sample is maintained at least 2000 s at each temperature of measurement and then cooled down to the following one at a rate of about 3 °C/min.

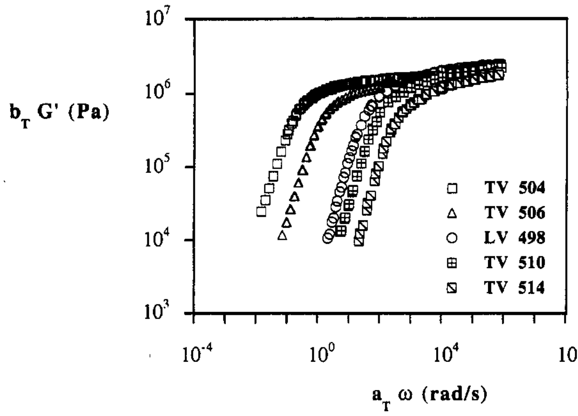

Figure 2. Storage moduli $G'(\omega)$ in the terminal and plateau zones of polybutadiene samples (molecular characterization in Table 1). The reference temperature T_r is 25 °C.

Table 3. Rheological Data of Linear Polybutadienes from the Literature

	$A \times 10^{13}$ (at 25 °C)	B (at 25 °C)	$J_e^0 \times 10^6$ (Pa)	$G_N^0 \times 10^{-6}$ (Pa)
Rochefort et al.[22]	5.2	3.4	2.1 ± 0.2	1.3
Marin et al.[23]		3.4	1.85	
Raju et al.[24]			1.81	1.18
Struglinski et al.[25]	3.6	3.41	1.8−2.1	1.2
Colby et al.[26]	4	3.41	1.6−2	1.15
Baumgaertel et al.[30]		3.4		1.2−1.4
Berger and Meissner[28]	5.2	3.4	1.6−3.77	

Results

Terminal Zone. The linear viscoelastic properties of narrow molecular weight distribution polybutadienes have been fairly well studied in the terminal and the rubbery zones by Graessley and co-workers.[19,22-27] Only the main results relevant to this present study will be briefly recalled here. The zero-shear rate viscosity determined by:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{7}$$

was found to obey a power law for high molecular weight ($M_w > 5000$):

$$\eta_0 = A M_w^{\ B} \tag{8}$$

The loss moduli G'' obtained show a linear variation in the terminal zone, allowing the determination of η_0. Our data (Table 2) confirm the values obtained by Rochefort et al.[22] and Berger and Meissner[28] and others (see Table 3) with, at 25 °C:

$$A = 4.9 \times 10^{-13}\ (\eta_0 \text{ in Pa·s and } M_w \text{ in Da})$$

and

$$B = 3.41$$

The recoverable shear compliance obtained at low frequencies:

$$J_e^{\ 0} = \lim_{\omega \to 0} \frac{G'(\omega)}{G'(\omega)^2 + G''(\omega)^2} \tag{9}$$

was found to be virtually molecular weight independent for $M_w > 11\,900$, and our results agree with these findings (see Table 3).

Calculated values of the plateau modulus G_N^0, obtained by numerical integration over the terminal loss modulus peak:

$$G_N^{\ 0} = \frac{2}{\pi} \int_{-\infty}^{+\infty} G''(\omega)\, \mathrm{d} \ln \omega \tag{10}$$

vary slightly around the value of 1.19×10^6 Pa reported by Ferry,[8] which is closer to our results. This leads to an apparent molecular weight between entanglements:

$$M_e = \varrho RT / G_N^{\ 0} \tag{11}$$

on the order of 1850.

As for other linear polymers, the time-temperature superposition principle was found to apply at temperatures well above T_g when taking into account not only a horizontal shift factor $(a_T)_\eta$ but also a vertical shift factor b_T due to variations in density.[8] We give in Figures 2 and 3 the dynamic moduli master curves for a reference temperature of 25 °C so obtained for all our samples.

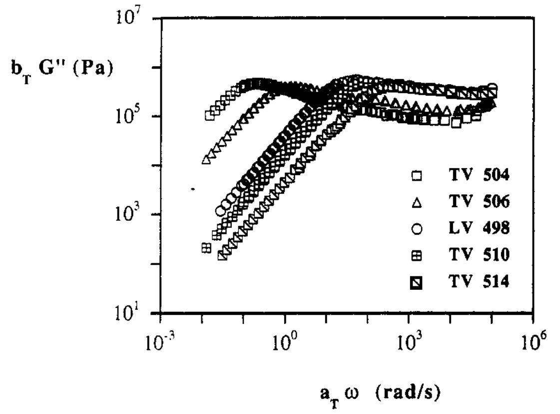

Figure 3. Loss moduli $G''(\omega)$ corresponding to the data in Figure 2.

The temperature dependence of $(a_T)_\eta$ is usually analyzed within the framework of either the Adam–Gibbs[29] theory or the free volume theory.[8] The Adam–Gibbs theory gives a nonexponential form for the temperature variation of the relaxation time (previously known as the Vogel–Fulcher–Tamman–Hesse (VFTH) empirical equation):

$$\ln \lambda = A + B/(T - T_0) \tag{12}$$

The free volume theory gives the Doolittle equation:

$$\ln \frac{\lambda}{\lambda_r} = \frac{1}{\alpha_r(T - T_0)} - \frac{1}{\alpha_r(T_r - T_0)} \tag{13}$$

where α_r is the thermal expansion coefficient of the free volume and T_r the reference temperature.

An equivalent form is the Williams–Landel–Ferry (WLF) equation:

$$\log \frac{\lambda}{\lambda_r} = -\frac{C_1(T - T_r)}{C_2 + T - T_r} \tag{14}$$

Although the theories are different, eqs 12 and 14 are equivalent provided that

$$C_2 = T_r - T_0$$

and

$$C_1 = \frac{B}{2.303(T_r - T_0)} \tag{15}$$

When T_g is chosen as the reference temperature, the coefficients in the WLF equation are usually termed C_{1g} and C_{2g}. In order to emphasize that the original data are obtained from the terminal to rubbery zone, we will use the notation $[C_{1g}]_\eta$ and $[C_{2g}]_\eta$.

Carella et al.[19] obtained shift factors in the range $\{T_g + 55\ °C, T_g + 150\ °C\}$ for polybutadienes of different molecular mass and microstructure, with T_g varying from −90 to 0 °C. These authors were able to obtain an a_T master curve for polybutadienes irrespective of the microstructure and the molecular weight with:

$$[C_{1g}]_\eta = 14 \quad \text{and} \quad [C_{2g}]_\eta = 40$$

Baumgaertel et al.[30] obtained slightly different values in the range $\{T_g + 15\ °C, T_g = 150\ °C\}$:

$$[C_{1g}]_\eta = 10.4 \quad \text{and} \quad [C_{2g}]_\eta = 79$$

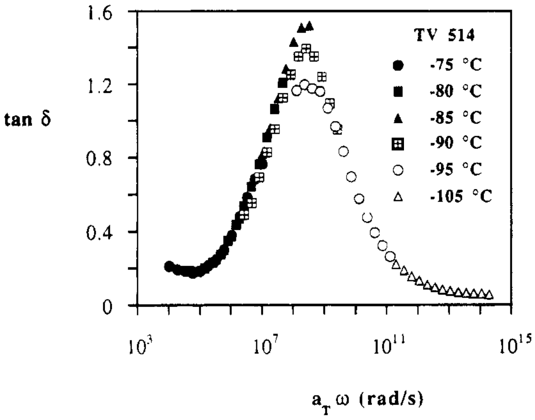

Figure 4. tan δ (=G''/G') in the softening zone plotted versus the reduced frequency for the sample TV514 M_w/M_e = 27). The reference temperature T_r is 25 °C.

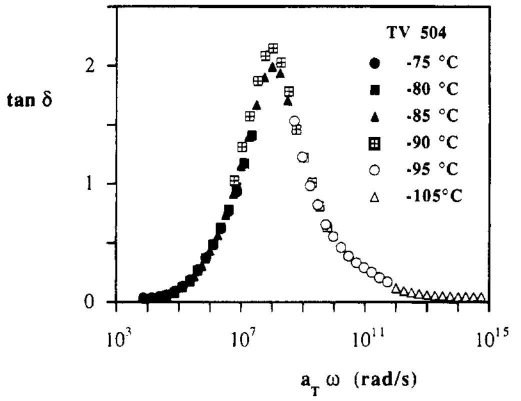

Figure 5. tan δ (=G''/G') for the sample TV504 (M_w/M_e = 251) as in Figure 4. The reference temperature T_r is 25 °C.

As Carella et al.,[19] we found that taking T_g as the reference temperature produces an a_T master curve. Our WLF coefficients determined in the range $\{T_g + 35\ °C, T_g + 165\ °C\}$ are close to Baumgaertel's ones[30] with:

$$[C_{1g}]_\eta = 11.4 \quad \text{and} \quad [C_{2g}]_\eta = 96 \tag{16}$$

Softening and Glassy Zones. Although mechanical behavior of un-cross-linked polybutadienes have been extensively studied in the terminal and rubber zones, we are not aware of dynamic data covering the softening and the glassy zones. The only exceptions are due to Roland and Ngai[31] and Colby et al.[26] In the first case, storage moduli measurements are not reported, and for the secound group, the storage moduli data are suspected to be wrong in the transition zone as stated by the authors themselves.

We will first examine our data in light of the contradictory results upon the validity of thermorheological simplicity within the softening zone obtained so far.

Cavaillé et al.[10] claimed that no master curve could be obtained for a narrow distribution polystyrene in the softening zone. This observation was done on the basis of isothermal graphs of tan δ. Indeed, since tan δ is plotted on a linear scale, such plots are more sensitive than the dynamic moduli log–log plots to the eventual inadequacy of time–temperature superposition.

In Figures 4 and 5, we present our results obtained for the lowest and highest molecular weights when plotted versus a reduced frequency $a_T\omega$ with a reference temperature of 25 °C. One can observe that, similarly to findings of Cavaillé et al.[10] for polystyrene, the lowest molecular weight polybutadiene TV514 (M_w/M_e = 27)

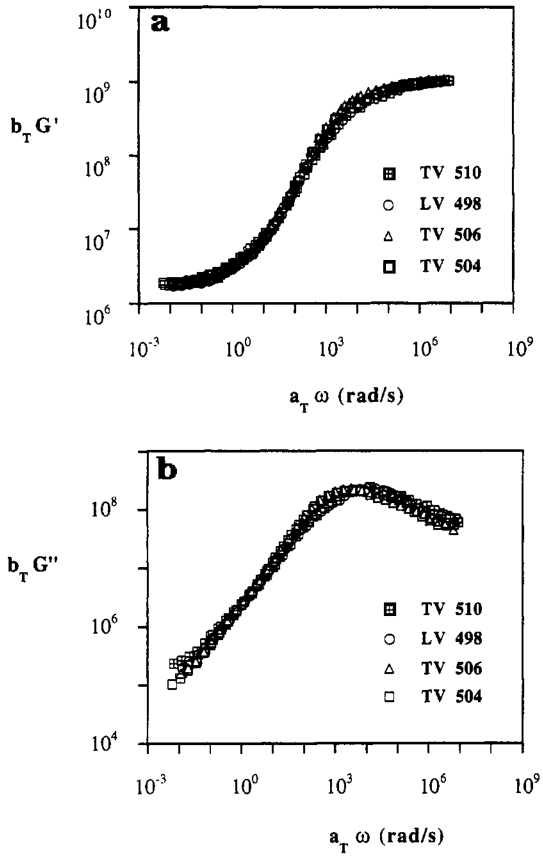

Figure 6. (a) Storage moduli $G'(\omega)$ in the softening and glassy zones of polybutadiene samples (molecular characterization in Table 1). The reference temperature T_r is −85 °C. (b) Loss moduli $G''(\omega)$ corresponding to the data in Figure 6a.

presents a gradual change with temperature in the shape of the tan δ curve. However, the variation with temperature of the loss tan δ peaks is in the reverse order to that observed by Cavaillé et al.[10] It is of interest to note that the polystyrene used by Cavaillé et al. had a lower M_w/M_e ratio (=5.5) than our samples. Instead, for our highest molecular weight polybutadiene TV504 (M_w/M_e = 251) the changes with temperature are weaker and differences observed are, in this case, on the order of the precision of the measurement. A similar pattern is observed for the other samples with the exception of the TV514. This suggests the hypothesis that the nonadequacy of time−temperature superposition would be observed only for low M_w/M_e ratios. One possible explanation, within the framework of Ngai's coupling model, is that for low M_w/M_e ratios the two processes corresponding to the α-relaxation and terminal behavior are not well separated in the time domain as in the case of high molecular weight polymers. Then, experimental data in the softening zone would reflect the segmental relaxation alone only in the case of a high M_w/M_e ratio.

Assuming that the principle of time−temperature superposition is valid, we obtained the master curves at T_r = −85 °C for G' and G'' as reported in parts a and b of Figure 6. Unreduced data for the sample TV504, chosen as an example, are shown in parts a and b of Figure 7.

Discussion

A check of the coupling model implies the relations (1), (5), and (6).

In Figure 8 we present reduced loss moduli data obtained for the sample TV506 chosen as an example. The curve corresponds to the prediction of eq 1 with β_η = 0.59, which is the value given by eq 6. As observed, the agreement is excellent near the peak and at low frequencies.

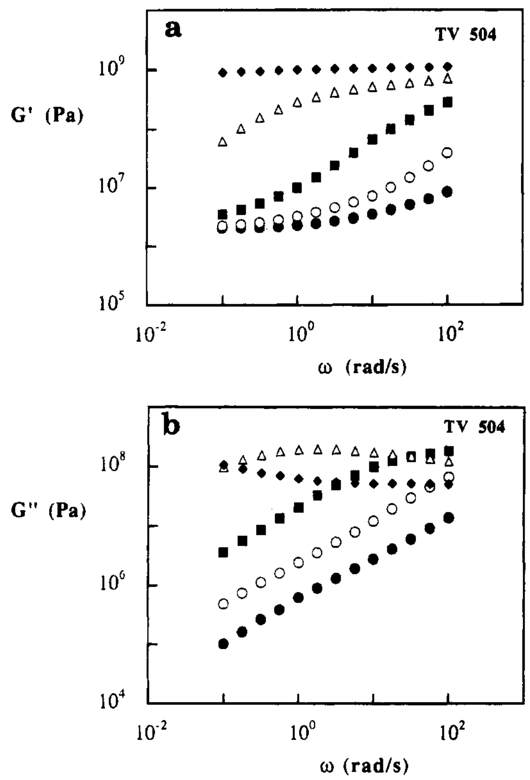

Figure 7. (a) Unreduced storage moduli for the sample TV504, corresponding to the data in Figure 6a. The reference temperature T_r is − 85 °C. (●) −80 °C; (○) −85 °C; (■) −90 °C; (△) −95 °C; (◆) −105 °C. (b) Unreduced loss moduli for the sample TV504, corresponding to the data in Figure 6b. The reference temperature T_r is −85 °C. (●) −80 °C; (○) −85 °C; (■) −90 °C; (△) −95 °C; (◆) −105 °C.

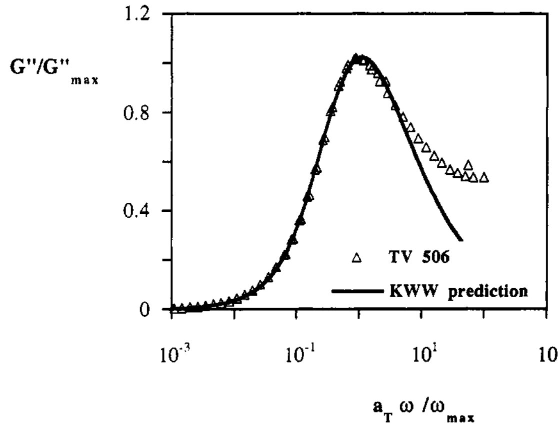

Figure 8. Reduced loss moduli $G''(\omega)/G''_{max}(\omega_{max})$ in the terminal zone plotted versus reduced frequency $a_T\omega/\omega_{max}$ for the sample TV506 (open triangles). The continuous line represents the prediction of eq 1 with β_η = 0.59.

For the glassy zone we could determine an a priori range for β_α resulting from various previous studies.[31−33]

Recently, Roland and Ngai[31] have studied polybutadienes of various vinyl contents. They claimed that in the glass transition region the shape of the loss uniaxial extension modulus was correctly predicted by the KWW function. They also found that β_α varies linearly with vinyl content. For a vinyl content of 11% (as in our samples) the interpolation of their data would give a value of 0.46 ± 0.01. On the other hand, Zorn, Frick,

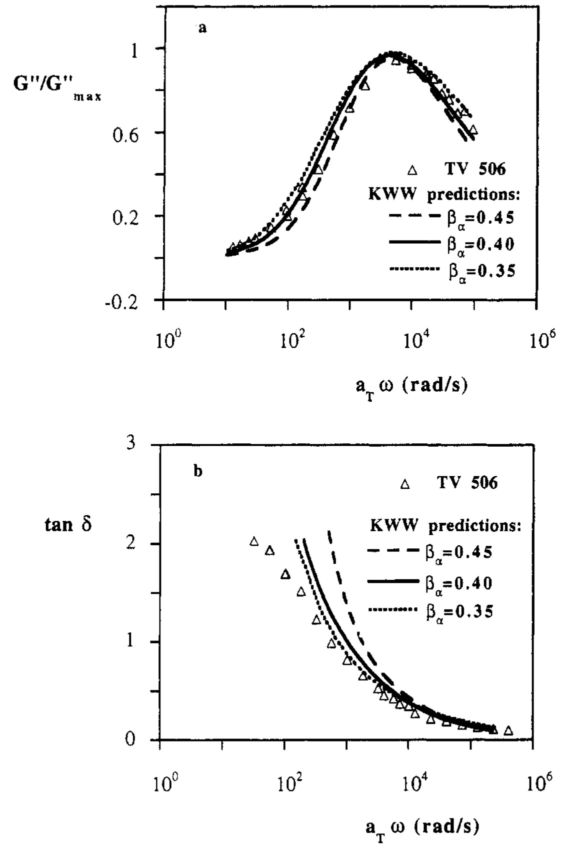

Figure 9. Reduced loss moduli (a) and tan δ (b) in the glassy zone, for the sample TV506 (open triangles), plotted versus reduced frequency. The reference temperature is −85 °C. The lines represent the predictions of eq 1 for various values of parameter β_α.

and co-workers[32,33] reported neutron scattering experiments on a polybutadiene with a vinyl content of 7%. The observed relaxation function in the case of coherent scattering corresponds to Kohlrausch behavior with an exponent depending on the momentum transfer Q:β_α (Q = 1.48 Å^{-1}) = 0.45, β_α (Q = 1.88 Å^{-1}) = 0.37. However, for incoherent scattering a value of 0.3 was obtained.

Taking into account this scatter in the reported values of β_α, we have plotted in Figure 9 the prediction of eq 1 in the glassy zone, with values of β_α ranging from 0.35 to 0.45, together with experimental data obtained for the TV506 sample. It should be noted that most of the β_α values reported in the literature are based on loss moduli fit only. In such a way a value of 0.45 similar to findings of Roland and Ngai[31] would be acceptable. However, the best fit of tan δ is obtained for β_α = 0.35. A value of 0.4 is the best compromise when taking into account the real and imaginary parts of the complex modulus.

Finally, in Figure 10 we have plotted the prediction of eq 5 along with the apparent shift factors a_T obtained by the empirical procedure described in the previous paragraph with T_r = 25 °C as the reference temperature.

The shift factors obtained for temperatures well above T_g were assumed to be free from segmental contribution and thus identical to $(a_T)_\eta$. As stated in the previous paragraph, they obey a WLF equation with the set of constant (16) (continuous line in Figure 10). The dotted lines correspond to $(a_T)_\alpha$ predicted by eq 5 with β_η = 0.59 and the same values of β_α as in Figure 9. The agreement with the shift factors obtained well below T_g is satisfactory for β_α = 0.40. This result supports the prediction of Ngai's model on the existence of a correlation between the shape of the relaxation function and the temperature dependence of the shift factors. It should be noted that in a neighborhood around T_g the apparent or empirical shift factors result from a compromise between the two contributions.

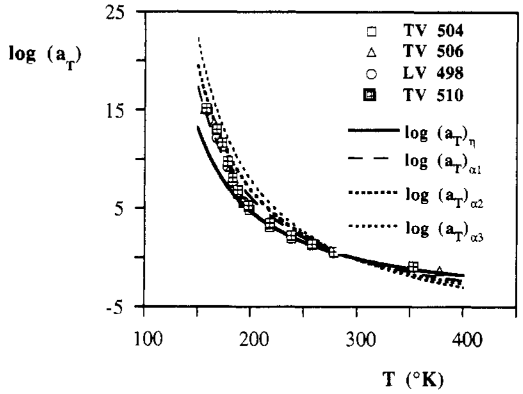

Figure 10. Symbols: apparent shift factors a_T obtained from the terminal zone to the glassy state; the reference temperature is 25 °C. The solid curve corresponds to the WLF fit for shift factors obtained well above T_g (eqs 14 and 16). The dotted lines correspond to the prediction of eq 5 with the values of β_α used in Figure 9: thus, the α1 index corresponds to β_α = 0.45, α2 to β_α = 0.40, α3 to β_α = 0.35.

Conclusions

We have been able to obtain, using the same technique, the loss and storage shear moduli from the terminal to the glassy zones. The KWW relaxation function derived from the coupling model of Ngai and co-workers has been shown to represent fairly well the loss moduli peaks in the terminal to rubbery and softening to glassy zones. This agreement is particularly remarkable in the terminal zone where the KWW exponent is not adjustable but derived from the well-known viscosity–molecular weight scaling law. Nevertheless, the model should be improved to obtain a better representation of both storage and loss moduli variations especially in the glassy and softening zones.

In the glassy zone a KWW exponent of 0.4 correlates well with those obtained on polybutadienes from NMR or uniaxial extension measurements. Moreover, the shape of the loss moduli peak was found to be independent of the temperature at high entanglement density.

Finally, the coupling theory leads to a correlation between the frequency and temperature behaviors. We have shown that our results are consistent with this prediction. This leads to the conclusion that polybutadienes do not show thermorheological simplicity. The apparent shift factors obtained do not obey a single WLF law because of an apparent transition between segmental and whole chain relaxation behavior. This transition is due to the limited range of frequencies available at a given temperature which precludes the simultaneous observation of glassy and terminal zones. It should be noted that this phenomenon takes place in the vicinity of T_G. Pure segmental behavior could be obtained only in the case of high molecular weight monodisperse polymers and well below T_g. Pure terminal behavior is obtained above T_g + 30 °C.

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References and Notes

(1) Plazek, D. J.; Zheng, X. D.; Ngai, K. L. *Macromolecules* **1992**, *25*, 4920.
(2) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(3) Williams, G. *J. Non-Cryst. Solids* **1991**, *131*–133, 1.
(4) Ngai, K. L.; Plazek, D. J. *J. Polym Sci., Polym. Phys. Ed.* **1985**, *23*, 2159.
(5) Doi, M.; Edwards, S. F. *The theory of polymer dynamics*; Clarendon Press: Oxford, U.K., 1986.
(6) Bird, R. B.; Armstrong, R. C.; Hassager, O.; Curtiss, C. E. *Dynamics of polymeric liquids*, 2nd ed.; Wiley: New York, 1987.
(7) Ngai, K. L.; Rajagopal, A. K.; Teitler, S. *J. Chem. Phys.* **1988**, *88* (8), 5086.
(8) Ferry, J. D. *Viscoelastic properties of polymers*, 3rd ed.; Wiley: New York, 1980.
(9) Colmenero, J. *J. Non-Cryst. Solids* **1991**, *131–133*, 860.
(10) Cavaillé, J.-Y.; Jourdan, C.; Perez, J.; Monnerie, L.; Johari, G. P. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1235.
(11) Boese, D.; Kremer, F. *Macromolecules* **1990**, *23*, 829.
(12) Zetsche, A.; Kremer, F.; Jung, W.; Schulze, H. *Polymer* **1990**, *31*, 1883.
(13) Colmenero, J.; Alegria, A.; Santangelo, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 407.
(14) Plazek, D. J. *J. Non-Cryst. Solids* **1991**, *131–133*, 836.
(15) Ngai, K. L. In *Disorder Effects on Relaxational Processes*; Richert, R., Blumen, A. Eds.; Springer-Verlag: New York, 1994; p 89.
(16) Ngai, K. L.; Schönhals, A.; Schlosser, E. *Macromolecules* **1992**, *25*, 4915.
(17) Ngai, K. L.; Plazek, D. J. *J. Polym Sci., Part B: Polym. Phys.* **1986**, *24*, 619.
(18) Busnel, J. P.; Degoulet, C.; Nicolai, T.; Woodley, W.; Patin, P., to be published.
(19) Carella, J. M.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 2775.
(20) McKenna, G. *J. Res. Natl. Stand. Technol.* **1994**, *99*, 169.
(21) Pérez, J.; Cavaillé, J. Y.; Diaz-Calleja, R.; Gomez-Ribelles, J. L.; Monleon-Pradas, M.; Ribes-Greus, A. *Makromol. Chem.* **1991**, *192*, 2141.
(22) Rochefort, W. E.; Smith, G. G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1197.
(23) Marin, G.; Menezes, E. V.; Raju, V. R.; Graessley, W. W. *Rheol. Acta* **1980**, *19*, 462.
(24) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1668.
(25) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630.
(26) Colby, R. H.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2226.
(27) Struglinski, M. J.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1988**, *21*, 783.
(28) Berger, L.; Meissner, J. *Rheol. Acta* **1992**, *31*, 63.
(29) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43* (1), 139.
(30) Baumgaertel, M.; De Rosa, M. E.; Machado, J.; Masse, M.; Winter, H. H. *Rheol. Acta* **1992**, *31*, 75.
(31) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 5315.
(32) Zorn, R.; Richter, D.; Frick, B.; Farago, B. *Physica A* **1993**, *201*, 52.
(33) Frick, B.; Richter, D.; Zorn, R.; Fetters, L. J. *J. Non-Cryst. Solids* **1994**, *172–174*, 272.

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