α- and β-Relaxations in Neat and Antiplasticized Polybutadiene

R. CASALINI,[1] K. L. NGAI,[2] C. G. ROBERTSON,[2] C. M. ROLAND[2]

[1] INFM e Dipartimento di Fisica, Universitá di Pisa, Via Buonarroti 2, I-56127, Pisa, Italy

[2] Naval Research Laboratory, 4555 Overlook Avenue, NW, Washington, DC 20375-5342

ABSTRACT: Dielectric spectroscopy was carried out to measure the α-relaxation (local segmental motion) and the higher frequency, secondary relaxation (β-mode) in 1,4-polybutadiene, both neat and containing a nonpolar diluent, mineral oil. The α-relaxation shifted to lower frequencies (antiplasticization) in the presence of the diluent, suggesting the glass temperature of the latter is higher than the T_g of the polymer (i.e., >187K). The T_g of neat mineral oil cannot be determined directly, due to crystallization. While the diluent increased the magnitude of the α-relaxation times, it had no effect on the β-relaxation. Moreover, neither the shape of the α-relaxation function nor its temperature dependence was influenced by the diluent. From this we conclude that the main effect of the mineral oil was to increase the local friction, without changing the degree of intermolecular cooperativity of the molecular motions. We also find that near the glass temperature, there is rough agreement between the time scale of the secondary relaxation process and the value of a noncooperative relaxation time estimated from theory. This approximate correspondence between the two relaxation times also holds for 1,2 polybutadiene. However, the β-process cannot be identified with the noncooperative α-relaxation, and the relationship between them is not quantitative. © 2000 John Wiley & Sons, Inc.* J Polym Sci B: Polym Phys 38: 1841–1847, 2000

Keywords: polybutadiene; mineral oil; dielectric spectroscopy; glass transition; α-relaxation; β-relaxation; segmental relaxation; fragility; antiplasticization

INTRODUCTION

The presence of solvent can affect the dynamics of polymer chains in a number of ways. Spatial variation of the local composition gives rise to a distribution of relaxation behaviors, and consequently an inhomogeneously broadened relaxation function.[1–5] Small-molecule diluents can alleviate the severity of constraints on local motion, thereby reducing the degree of intermolecular cooperativity associated with the local mo-

tion.[6–8] Alteration of the local friction, for example, through changes in the available free volume or the configurational entropy,[9–12] can change the dynamics of the chain molecules, by what might be called a "T_g-effect". In this article we describe dielectric spectroscopy measurements of the primary and secondary relaxations in a polybutadiene (1,4-PB), of primarily 1,4-microstructure, both neat and containing a nonpolar diluent.

Measurements carried out in the vicinity of T_g reveal how diluent affects the local segmental motion. By obtaining data at lower temperatures, the effect on the higher frequency, secondary relaxation (β-mode) can be observed. The β-process occurs generally in glass-formers of diverse chemical structure, and has properties markedly different from the α-relaxation. For example, the

secondary relaxation usually exhibits an Arrhenius temperature dependence of its relaxation time, $\tau_\beta(T)$, compared to the much stronger temperature dependence of $\tau_\alpha(T)$. The difference in magnitude between $\tau_\beta(T)$ and $\tau_\alpha(T)$ can be substantial near T_g, but decreases with increasing temperature. The two quantities show a tendency to coincide at some higher temperature, referred to as the merging temperature.[13]

In some cases, the secondary process can be assigned unambiguously to motion of a side group on the polymer chain. In this case, the β-relaxation is decoupled from the α-relaxation, and its behavior can be readily interpreted. More interesting are β-processes occurring in glass-formers that have no side groups; these also tend to merge with the α-relaxation. This type of β-process was found by Johari and Goldstein in small molecule glass-formers.[14] 1,4-polybutadiene, in which all carbon atoms reside in the backbone, has a β-process that belongs to this interesting category. Analysis of the molecular mechanism underlying such β-processes can possibly shed light on the cooperative motions associated with the α-relaxation.

Neutron spin echo experiments led to the conclusion that the β-process in 1,4-PB is intermolecularly noncooperative, involving rotation of *cis* and *trans* units.[15] Therefore, a combined study of the α- and β-relaxations in polybutadiene is potentially quite useful, as recognized by various groups.[14–17] Herein, we are interested in probing the correlation between the α- and β-processes, and any effect therein of dilution of the polymer chains. Among the polybutadienes, the β-relaxation in 1,4-polybutadiene has the strongest dielectric strength, and thus is well suited for such a study. We also compare our results to the properties of the α- and β-processes in 1,2-polybutadiene.

EXPERIMENTAL

The 1,4-polybutadiene (Diene 35NF) was obtained from the Bridgestone/Firestone Company. The mineral oil was Lubinol, a U.S. Pharmacopia grade light paraffin oil. It was incorporated into the polybutadiene at 14% by weight using a Brabender mixer.

Isothermal dielectric spectra were obtained using a time domain spectrometer (Imass Inc.) over a frequency range from 10^{-4} to 10^4 Hz. The sample cell consisted of parallel plates 25 mm in diameter. Sample thicknesses were from 0.2 mm to 0.4 mm. The temperature was controlled to ±0.1 K by means of a Delta Design Model 9023 oven, with the samples maintained in a nitrogen atmosphere during the measurements.

RESULTS

The relaxation in glass-forming liquids is characterized by a nonexponential time dependence of the primary relaxation process (α-process), which can be described by a correlation function having the Kohlrausch–Williams–Watts (KWW) stretched exponential form[18,19]

$$\varepsilon(t) = \varepsilon_0 e^{-(t/\tau_\alpha)^\beta} \tag{1}$$

in which τ_α is the relaxation time and β the Kohlrausch exponent for the α-process. To analyze the dielectric relaxation in the frequency domain, the Fourier transform of the time derivative of the KWW function is often used, as well as other empirical functions, such as the Havriliak–Negami equation.[20]

The relaxation time of the α-process, τ_α, is characterized by a rapid increase as the liquid is cooled toward the glass transition. For dynamics, it is customary to define the glass temperature, T_g, as the temperature at which τ_α equals 10^2 s; that is, close to the time scale of typical differential scanning calorimetry measurements. The behavior of τ_α near T_g is usually described using the Vogel–Fulcher–Tammann–Hesse (VFTH) equation

$$\tau_\alpha = \tau_{\alpha,0} e^{DT_0/(T-T_0)} \tag{2}$$

where $\tau_{\alpha,0}$, D and T_o are material constants. Deviations from this equation are not uncommon when data are obtained over a wide range of temperatures and frequencies.[21,22]

Contrary to the local segmental dynamics, the relaxation time of the β-process generally exhibits an Arrhenius temperature dependence

$$\tau_\beta = \tau_{\beta,\infty} e^{(E_\beta/kT)} \tag{3}$$

where E_β is the activation energy and $\tau_{\beta,\infty}$ a constant. Typically, E_β is less than one eV ($\approx$10 kcal/mol) and $10^{-16} < \tau_{\beta,\infty} < 10^{-13}$ s, suggesting that the β-relaxation is related to simple, local motions.

α-Relaxation in PB

It has long been known [23] that polybutadienes show a monotonic increase of T_g with vinyl content. Although several groups have studied the local segmental dynamics (α-relaxation) of both 1,4- and 1,2-PB,[15–17,24–33] interpretation of the shape of the dielectric relaxation function in 1,4-PB is complicated by overlapping of the α- and β-peaks. This complication has led to conflicting results concerning the value of the Kohlrausch β parameter in eq 1, for the α-relaxation in 1,4-PB. The overlap gives rise to an apparent decrease of β with increasing temperature,[33] in contrast with the usual behavior of glass-formers. A recent comprehensive analysis of previous mechanical and dielectric spectroscopy studies of the local segmental motion in 1,4-PB, along with some new results, demonstrated that decreasing vinyl content is associated with a narrower dispersion or larger value of the Kohlrausch exponent β.[34]

Representative dielectric constant and loss spectra are shown in Figure 1 for 1,4-PB both neat and blended with 14% mineral oil. Because of uncertainties concerning sample thickness, the absolute values for the ordinate scale are only approximate. The peak shapes are virtually identical, although as seen, the addition of diluent shifts the dispersion to lower frequency (antiplasticization). A most probable relaxation time can be defined as the reciprocal of the circular frequency of the maximum in the loss modulus, $\tau_\alpha = 1/\omega_{max}$. This gives different values than obtained by fitting the spectra to a function such as eq 1, especially at higher temperatures where the α- and β-processes are closer. The most probable relaxation times are shown as the filled symbols in Figure 2. The values for the neat polymer suggest a somewhat higher vinyl content (and hence higher T_g) than the 1,4-PB used in some prior studies.[16] It is difficult to measure low 1,2-contents accurately, and absolute determinations differ according to the method of analysis.

The antiplasticization effect of the diluent is reflected in a higher calorimetric glass-transition temperature measured for 1,4-PB containing 14% mineral oil, T_g = 189.0 K, compared with neat 1-4-PB, T_g = 186.8 K. The implication is that the mineral oil itself has a higher T_g than the neat polybutadiene. This is difficult to verify directly, because the material crystallizes, at roughly 238 K, during cooling towards T_g. As a crude estimate, we can use the "rule-of-thumb" that the glass temperature is two-thirds times the melting
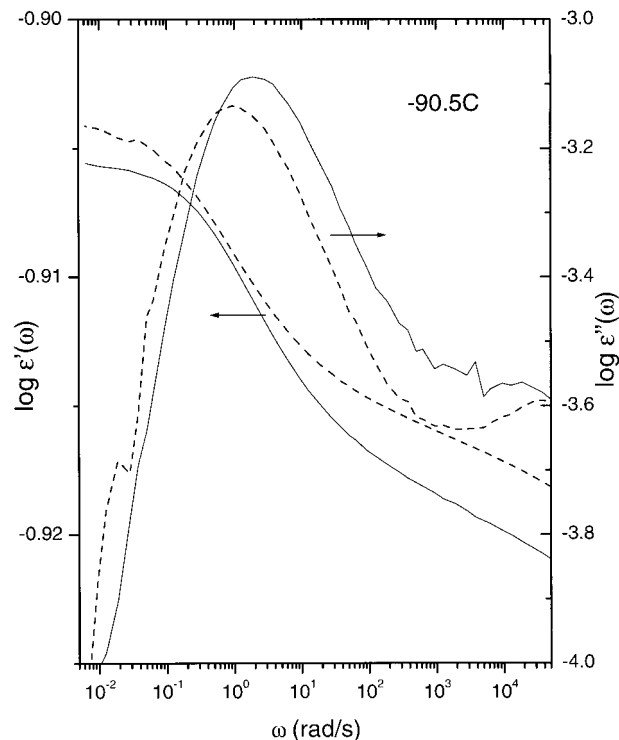

Figure 1. Representative dielectric spectra for the α-process in 1,4-PB neat (solid lines) and blended with 14% mineral oil (dashed lines) at the indicated temperature. The absolute values for the ordinate scale are only approximate, due to uncertainties in sample dimensions.

point.[35] We determined the latter by scanning calorimetry to be about 273 K, yielding T_g = 182 K, which is below the glass temperature of the polymer. More consistent with the observed antiplasticization of the α-process is the glass temperature of 192 K reported for polyethylene,[36,37] although this should be higher than the T_g of mineral oil due to the effect of molecular weight.

There have been several reported mixtures, in which addition of a *higher* T_g component *reduces* the relaxation time,[6–8,38,39] and at least one instance in which addition of a *lower* T_g component *slows down* the relaxation.[40,41] Such anomalies arise when there is a large difference in intermolecular cooperativity between the components, as reflected in the shape of their segmental relaxation functions or their fragility. We believe such an anomaly is unlikely herein, given the minimal change in the dielectric loss dispersion (Fig. 1), and the fact that 1,4-PB and polyethylene (higher molecular weight paraffin) are both relatively less fragile glass-formers.[42]

The τ_α are well described by eq 2, as shown by the solid lines in Figure 2. For neat 1,4-PB, the
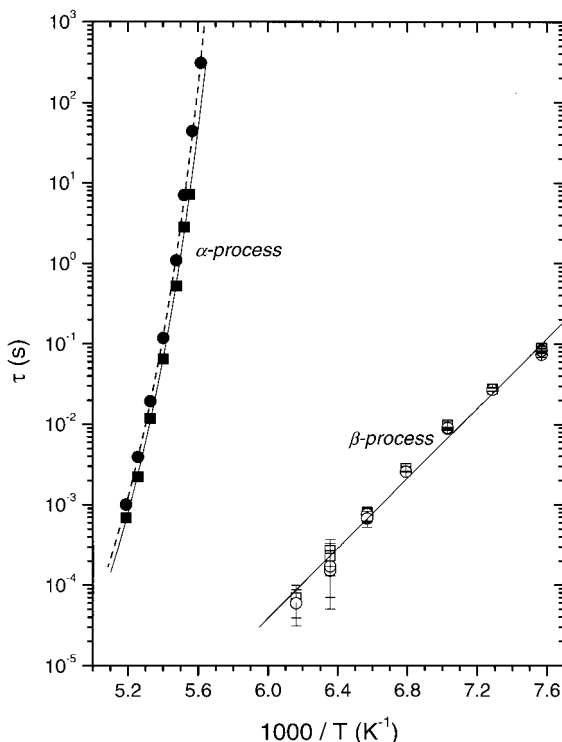
Figure 2. Relaxation times for local segmental motion (filled symbols) and for the secondary relaxation (hollow symbols) in 1,4-PB neat (squares) and blended with 14% mineral oil (circles).

obtained VTF parameters are $\log \tau_{\alpha,0} = -7.89$, $D = 1.91$ and $T_o = 164.5$ K, while for the blend with mineral oil, $\log \tau_{\alpha,0} = -7.67$, $D = 1.91$, and $T_o = 164.7$ K. The data in Figure 2 indicate that dilution with mineral oil has minimal influence on the temperature dependence. If the diluent altered the intermolecular cooperativity (presumably making it less cooperative), the "strength parameter", D, would be expected to be different.[43–45] It is more common to characterize the temperature dependence using the inverse property, fragility, which is just the T_g-normalized temperature dependence.[43–45] In terms of the VTF parameters, fragility is given by [46]

$$m = \frac{DT_0}{T_g \ln(10)} \times (1 - T_0/T_g)^{-2} \quad (4)$$

As mentioned above, for dynamics it is more appropriate to define T_g in terms of the temperature at which the relaxation time assumes an arbitrary value, for example, $\tau_\alpha = 100$ s; this gives $T_g = 178.3$ and 178.8 K, respectively, for neat and diluted 1,4-PB. Equation 4 then yields for the

fragility, $m = 125 \pm 3$, essentially equal for the two samples. Since fragility is well established to correlate with the degree of intermolecular cooperativity of the segmental relaxation,[24,42,44,47–50] we can conclude that cooperativity is essentially unaffected by the presence of mineral oil. This is consistent with the negligible change in the shape of the α-relaxation function upon dilution (Fig. 1).

It is interesting to note that addition of 14% mineral oil decreased the dielectric strength by roughly 40% relative to that of neat PB. This variation is certainly larger than expected, and might suggest some reduction in orientability of the polybutadiene dipoles in the presence of the mineral oil. However, this would constitute a change of intermolecular cooperativity, at odds with the invariance of both the relaxation function and the temperature-dependence of τ_α (fragility).

β-Relaxation

The β-process occurs at higher frequencies or lower temperature than the α-relaxation. Representative dielectric loss peaks for the β-process at two temperatures are shown in Figure 3, in both the neat polybutadiene and the mixture. The curves through the data are fits to the Cole–Cole function.[51]

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + i\omega\tau)^\gamma} \quad (5)$$

It can be noted that the presence of diluent affects neither the shape (the parameter γ) nor position (τ_β) of the β-relaxation peak. The shape parameter, $\gamma = 0.24 \pm 0.03$, is slightly less than reported by Hofmann et al.[16]

The relaxation times, estimated for $T < T_g$ (where the contribution of the α-peak is negligible) by fitting to eq 5, are displayed in Figure 2. The temperature dependence is Arrhenius (eq 3), yielding a value for the activation energy, $E_\beta = 42$ kJ/mol. This can be compared to the apparent activation energy for the α-relaxation at T_g, calculated from the fragility using [43–45]

$$E_\alpha = \ln(10)RT_g m, \quad (6)$$

$E_\alpha = 430$ kJ/mol, which is an order of magnitude larger.

An aspect of interest herein is the correlation between $\tau_\beta(T_g)$ and the Kohlrausch exponent, β in
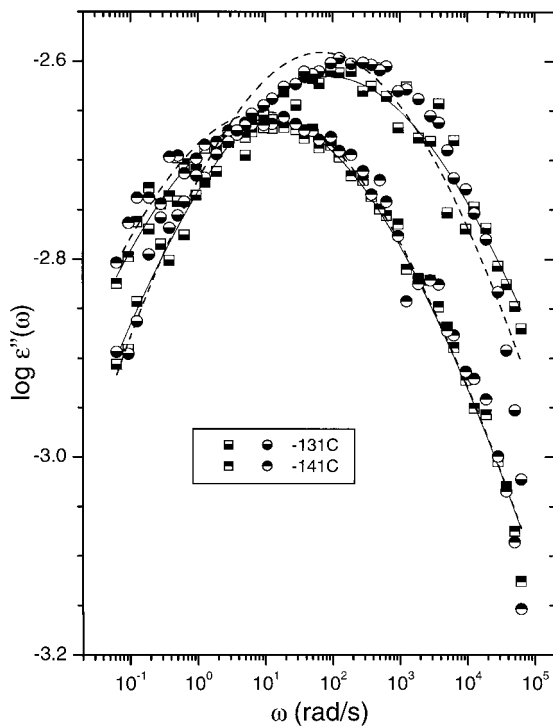
Figure 3. Representative dielectric spectra for the β-process in 1,4-PB neat (squares) and blended with 14% mineral oil (circles) at the indicated temperatures, along with fits to eq 4.

eq 1, for the α-relaxation function. The existence of a relationship between these quantities was noted for various glass-formers, including polymers.[52,53] Since there is no change in the breadth of the α-dispersion upon addition of the diluent, the implication of this correlation is no change in the relaxation time of the β-process, as is observed.

The relationship between $\tau_\beta(T_\beta)$ and the Kohlrausch exponent can be made more explicit through the coupling model.[52–54] This model provides an interpretation of the dynamics of the glass-formers, according to which intermolecular interactions became important only beyond a temperature-insensitive crossover time $t_c \approx 2$ ps.[55,56] For $t < t_c$, the molecular units relax independently, giving rise to an exponential correlation function, $\phi(t) = \exp(-\tau/\tau_0)$, where τ_o is the primitive (noncooperative) relaxation time for the α-process. Beyond t_c, intermolecular interactions (i.e., cooperativity) slow down the relaxation, whereupon the averaged correlation function assumes the form of eq 1. These relaxation times τ_α and τ_o for the α-process are related by [52–54]

$$\tau_0(T) = t_c^{1-\beta}\tau_\alpha(T)^\beta \qquad (7)$$

where the quantity 1-β is a measure of the degree of intermolecular cooperativity. A smaller value of β implies more cooperative dynamics, and thus a more pronounced slowing down of the relaxation process for $t > t_c$.

For polybutadienes, the β-relaxation has been shown to be noncooperative in nature[15] and thus we expect it to bear some resemblance to the primitive α-relaxation. However, these processes are evidently not the same, since the β-relaxation is not slowed down by intermolecular interactions at longer times.[52,53] This difference is especially clear near T_g, because at this temperature the primitive relaxation has effectively zero relaxation strength and cannot be experimentally observed, in contrast to the β-relaxation. Nevertheless, because both relaxation processes are free of the effects of cooperativity, intuitively they should not differ greatly, at least in the vicinity of T_g. This order of magnitude equality of $\tau_\beta(T_g)$ and $\tau_o(T_g)$ has been observed in various glass-formers.[52,53] In fact, the proximity of $\tau_\beta(T_g)$ and $\tau_o(T_g)$ underlies the general correlation found between $\log[\tau_\beta(T_g)]$ and the Kohlrausch exponent β.

For 1,4-PB, since τ_α changes upon addition of the mineral oil, τ_0 does also (eq 7). Nevertheless, τ_β is invariant to the presence of diluent (Fig. 2), contrary to the expected correlation between these quantities. However, the changes in τ_α due to dilution are not large, and moreover, there is no change in β with dilution. Accordingly, we extend this test of the proposed correlation to polybutadienes of different vinyl content, to determine whether $\tau_o(T)$ and $\tau_\beta(T)$ at least have comparable magnitudes for members within the same chemical family. To do this we compare at a given temperature, $\tau_\beta(T)$ determined experimentally to $\tau_o(T)$ calculated from eq 7, using with $t_c = 2 \times 10^{-12}$ s.[52,55,56] This requires knowledge of $\tau_\alpha(T)$, $\tau_\beta(T)$, and the Kohlrausch exponent from experimental data.

For 1,4-PB, we calculate $\tau_0(T_g)$, using eq 7 and the value of $\beta = 0.5$, established from both mechanical and dielectric spectroscopy.[24,25,34] For 1,2-PB, dielectric relaxation data of $\tau_\alpha(T)$ and $\tau_\beta(T)$ as reported by Hofmann et al.[16] are used, with $\tau_0(T_g)$ calculated using $\beta = 0.43$.[16,25,27,28] The results are displayed in Figure 4.

Using the temperatures for which $\tau_\alpha(T_\alpha)$ equal 10^2 s (T_g = 178 K and 268 K for 1,4- and 1,2-polybutadiene, respectively), the corresponding $\tau_o(T_g)$ at these temperatures are denoted by the horizontal lines in Figure 4. Note that these are roughly comparable to $\tau_\beta(T_g)$. Moreover, the temperature at which $\tau_\beta = \tau_0$ is within 2 degrees of
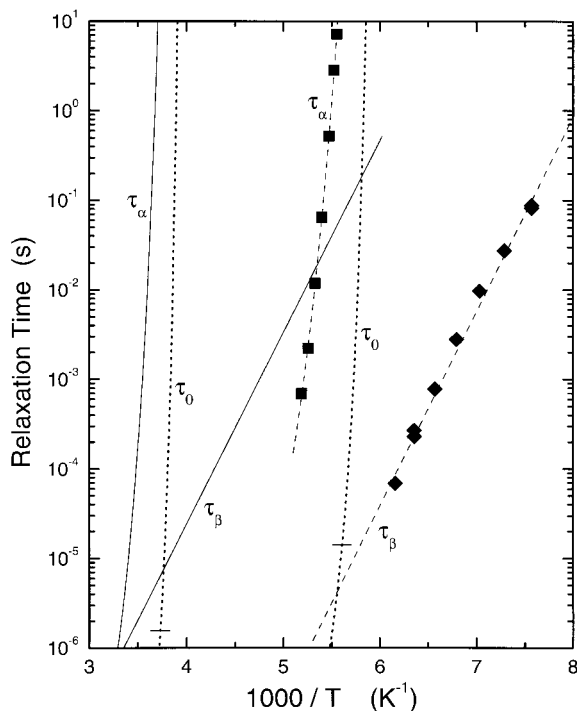
Figure 4. Relaxation times for the α- and β-processes, measured herein for 1,4-PB (dashed lines with symbols), and taken from ref. 16 for 1,2-PB (solid lines), along with the noncooperative α-relaxation times calculated from eq 6 (dotted lines). The short horizontal hatch marks represent the temperature at which τ_α = 100 s, which is in the vicinity of the temperature at which $\tau_\beta = \tau_o$ for each polybutadiene.

$T_{g\alpha}$ for both polybutadienes. Thus, while the two relaxation processes are not identical (for example, as seen in Fig. 4 they differ markedly in temperature dependence), there is a correspondence between the magnitudes of their relaxation times, at least in the vicinity of T_g and above.

CONCLUSIONS

An investigation on the effect of a nonpolar diluent (mineral oil) on the α- and β-relaxations in 1,4-polybutadiene was undertaken using dielectric spectroscopy. The main effect of the mineral oil was to increase the α-relaxation times, without change in the shape of the α-relaxation function or its temperature dependence. This result can be rationalized in terms of an increase in the local friction factor, with consequent slowing down of the segmental motion. There is no change in the degree of intermolecular cooperativity, as indicated by the invariance to diluent of both the

shape of the relaxation function and the fragility. The fact that the β-relaxation was unaffected by the presence of the mineral oil is consistent with the mechanism of the β-process involving only local, noncooperative motion of the chain.

Since addition of the diluent does not change the shape of the α-relaxation function, the correlation between the value of the Kohlrausch exponent for the α-relaxation function and the magnitude of τ_β near T_g [52,53] appears to hold for 1,4-PB, both with and without mineral oil. However, addition of the diluent causes deviation from the expected correspondence between the β-relaxation time and the noncooperative relaxation time, τ_o. Nevertheless, results for polybutadiene of both 1,4- and 1,2-chemical structure show τ_β and τ_o to be nearly equal at T_g. Clearly, this connection between τ_β and τ_o is on an empirical level, since there is no theory for the Johari–Goldstein β-relaxation. We can only say that τ_β is related to, but not identical with, the noncooperative relaxation time of the coupling model.

REFERENCES AND NOTES

1. Shears, M. S.; Williams, G. J Chem Soc Faraday Trans 2 1973, 69, 608.
2. Wetton, R. E.; MacKnight, W. J.; Fried, J. R.; Karasz, F. E. Macromolecules 1978, 11, 158.
3. Trask, C. A.; Roland, C. M. Macromolecules 1989, 22, 256.
4. Miller, J. B.; McGrath, K. J.; Roland, C. M.; Trask, C. A.; Garroway, A. N. Macromolecules 1990, 23, 4543.
5. McGrath, K. J.; Roland, C. M. J Non-Cryst Solids 1994, 172–174, 891.
6. Santangelo, P. G.; Ngai, K. L.; Roland, C. M. Macromolecules 1994, 27, 3859.
7. Santangelo, P. G.; Roland, C. M.; Ngai, K. L.; Rizos, A. K.; Katerinopoulos, H. J Non-Cryst Solids 1994, 172–174, 1084.
8. Roland, C. M.; Santangelo, P. G.; Ngai, K. L.; Meier, G. Macromolecules 1993, 26, 6164.
9. Lodge, T. P. J Phys Chem 1993, 97, 1480.
10. Schrag, J. L.; Stokich, T. M.; Strand, D. A.; Merchak, P. A.; Landry, C. J. T.; Radtke, D. R.; Man,

V. F.; Lodge, T. P.; Morris, R. L.; Hermann, K. C.; Amelar, S.; Eastman, C. E.; Smeltzly, M. A. J Non-Cryst Solids 1991, 131–133, 537.

11. Gisser, D. J.; Ediger, M. D. Macromolecules 1992, 25, 1284.

12. Fujita, H. Macromolecules 1993, 26, 643.

13. McCrum, N. G.; Read, B. E.; Williams, G. Anelastic and Dielectric Effects in Polymer Solids; Wiley: London, 1967.

14. (a) Johari, G. P.; Goldstein, M. J Chem Phys 1970, 53, 2372; (b) Johari, G. P. J Chem Phys 1970, 58, 1766.

15. Arbe, A.; Richter, D.; Colmenero, J.; Farago, B. Phys Rev E 1996, 54, 3853.

16. (a) Hofmann, A.; Alegria, A.; Colmenero, J.; Willner, L.; Buscaglia, E.; Hadjischristidis, N. Macromolecules 1996, 29, 129; (b) Arbe, A.; Buchenau, U.; Willner, L.; Richter, D.; Farago, B.; Colmenero, J. Phys Rev Lett 1996, 76, 1872.

17. Hansen, C.; Richert, R. Acta Polym 1997, 48, 484.

18. Kohlrausch, R. Pogg Ann Phys 1847, 12(3), 393.

19. Williams, G.; Watts, D. C. Trans Faraday Soc 1970, 66, 80.

20. Havriliak, S.; Negami, S. J Polym Sci C 1966, 14, 99.

21. Schneider, U.; Lunkenheimer, P.; Brand, R.; Loidl, A. Phys Rev E 1999, 59, 6924.

22. Corezzi, S.; Capaccioli, S.; Casalini, R.; Fioretto, D.; Paluch, M.; Rolla, P. A. Chem Phys Lett, submitted for publication.

23. Krauss, G.; Childers, W.; Gruver, J. T. J Appl Polym Sci 1967, 11, 158.

24. (a) Roland, C. M.; Ngai, K. L. Macromolecules 1991, 24, 5315; (b) Roland, C. M.; Ngai, K. L. Macromolecules 1992, 25, 1844.

25. Zorn, R.; McKenna, G. B.; Willner, L.; Richter, D. Macromolecules 1995, 28, 8552.

26. Roland, C. M. Macromolecules 1994, 27, 4242.

27. Colmenero, J.; Alegria, A.; Santangelo, P. G.; Ngai, K. L.; Roland, C. M. Macromolecules 1994, 27, 407.

28. Roland, C. M. Macromolecules 1995, 28, 3463.

29. Palade, L. I.; Verney, V.; Attané, P. Macromolecules 1995, 28, 7051.

30. Hofmann, A.; Alegria, A.; Colmenero, J.; Willner, L.; Buscaglia, E.; Hadjischristidis, N. Macromolecules 1996, 29, 129.

31. Reinhardt, L.; Fytas, G.; Fischer, E. W.; Willner, L. Acta Polym 1996, 47, 399.

32. Richter, D.; Frick, B.; Farago, B. Phys Rev Lett 1988, 61, 2465.

33. Zorn, R.; Mopski, F. I.; McKenna, G. B.; Willner, L.; Richter, D. J Chem Phys 1997, 107, 3645.

34. Robertson, C. G.; Roland, C. M. Macromolecules 2000, 33, 1262.

35. Sakka, S.; Ann Rev Mater Sci 1986, 16, 29.

36. Tobolsky, A. V.; Carlson, D. W.; Indicator, N. J Polym Sci 1961, 54, 175.

37. Boyer, R. F. Rubber Rev 1963, 34, 1301.

38. McGrath, K. J.; Roland, C. M. Macromolecules 1995, 28, 2982.

39. Roland, C. M.; Santangelo, P. G.; Baram, Z.; Runt, J. Macromolecules 1994, 27, 5382.

40. Alegria, A.; Telleria, I.; Colmenero, J. J Non-Cryst Solids 1994, 172–174, 961.

41. McGrath, K. J.; Roland, C. M. Rubber Chem Tech 1994, 67, 629.

42. Ngai, K. L.; Roland, C. M. Macromolecules 1993, 26, 6824.

43. Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. J Chem Phys 1993, 99, 4201.

44. Plazek, D. J.; Ngai, K. L. Macromolecules 1991, 24, 1222.

45. Böhmer, R.; Angell, C. A. Phys Rev B 1993, 48, 5857.

46. Hodge, I. M. J Non-Cryst Solids 1996, 202, 164.

47. Roland, C. M. Macromolecules 1992, 25, 7031.

48. Roland, C. M.; Ngai, K. L. Macromolecules 1992, 25, 5765.

49. Roland, C. M.; Ngai, K. L. Macromolecules 1992, 25, 363.

50. Ngai, K. L.; Roland, C. M.; O'Reilly, J. M.; Sedita, J. S. Macromolecules 1992, 25, 3906.

51. Cole, K. S.; Cole, R. H. J Chem Phys 1941, 9, 341.

52. Ngai, K. L. J Chem Phys 1998, 109, 6982.

53. Ngai, K. L. Phys Rev E 1998, 57, 7346.

54. Ngai, K. L. Macromolecules 1999, 32, 7140.

55. Colmenero, J.; Arbe, A.; Alegria, A. Phys Rev Lett 1993, 71, 2693.

56. Roland, C. M.; Ngai, K. L.; Lewis, L. J. J Chem Phys 1995, 103, 4632.