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On the dynamical mechanical behaviour of atactic polystyrene

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Data on tan ϕ against frequency, reported recently in the literature, which have been obtained for monodisperse atactic polystyrene in the frequency range 10^{-5} to $10\,\text{sec}^{-1}$ and temperature range 359 to 374 K, are discussed. It is shown that time–temperature superposition can be applied to the experimental curves, if they are normalized to account for the temperature dependence of the relaxation strength. Finally, a general discussion of the translation behaviour of the internal friction curves, particularly for a distribution of relaxation times, is presented.

1. Introduction

In a recent paper, which in what follows will be referred to as Paper I, Cavaille *et al.* [1] have presented data on the dynamical mechanical behaviour of monodisperse actactic polystyrene (mol. wt 98 000) in the frequency range 10^{-5} to $10\,\text{sec}^{-1}$ and temperature range 359 to 374 K. According to the authors, the time–temperature superposition of the entire data in the frequency range of overlap seems less than satisfactory in both the real and the imaginary components of the complex shear modulus, G' and G'', respectively. The lack of adequate superposition becomes pronounced in the tan ϕ (G''/G') plots. Moreover, according to Paper I, the tan ϕ plots provide a more discerning criteria for superposition than the G' and G'' spectra.

It is the purpose of this work to show that the tan ϕ against frequency curves, obtained at different temperatures and presented in Paper I, do in fact superpose under a translation parallel to the frequency axis, when the temperature dependence of the relaxation strength is taken into account. Furthermore, since scarce data have been reported in the literature on tan ϕ against frequency, particularly for high relaxation strengths, the curves reported in Paper I will be used as a base for a general discussion on the translation behaviour of the internal friction curves, particularly when a distribution of relaxation times is present.

2. Theory

2.1. *Single relaxation time*

The standard anelastic solid (SAS), which is characterized by three parameters, can be described in terms of Voigt unit by the equation (p. 47 of [2])

$$J_R\sigma + \tau_\sigma J_U\dot{\sigma} = \varepsilon + \tau_\sigma\dot{\varepsilon} \qquad (1)$$

where σ is the applied stress, ε is the strain, J_R and J_U are the relaxed and unrelaxed compliances, respectively, and τ_σ is the relaxation time at constant stress. The dot indicates a derivative with respect to the time. The dynamical response of such a solid is given by the real, (J_1) and the imaginary (J_2) components of the dynamic compliance (p. 47 of [2]), that is

$$J_1(\omega) = J_U + \frac{\delta J}{1 + \omega^2\tau_\sigma^2} \qquad (2)$$

$$J_2(\omega) = \frac{\delta J\omega\tau_\sigma}{1 + \omega^2\tau_\sigma^2} \qquad (3)$$

where $\omega = 2\pi f$ and f is the frequency of the applied stress of constant maximum amplitude, and

$$\delta J = J_R - J_U \qquad (4)$$

gives the magnitude of the relaxation of the compliance. Formulated in terms of a Maxwell unit, the SAS is described (p. 47 of [2]) by

$$\sigma + \tau_\varepsilon\dot{\sigma} = M_R\varepsilon + M_U\tau_\varepsilon\dot{\varepsilon} \qquad (5)$$

where M_R and M_U are the relaxed and unrelaxed moduli, respectively, and τ_ε is the relaxation time at constant strain. The dynamical response, under a sinusoidal strain of constant maximum amplitude, is given by the real (M_1) and the imaginary (M_2) components of the complex modulus (p. 47 of [2]), that is

$$M_1(\omega) = M_U - \frac{\delta M}{1 + \omega^2\tau_\varepsilon^2} = M_R + \frac{\delta M\omega^2\tau_\varepsilon^2}{1 + \omega^2\tau_\varepsilon^2} \qquad (6)$$

$$M_2(\omega) = \frac{\delta M\omega\tau_\varepsilon}{1 + \omega^2\tau_\varepsilon^2} \qquad (7)$$

where

$$\delta M = M_U - M_R \qquad (8)$$

gives the intensity of the relaxation for the modulus. Another dynamical quantity is the internal friction,

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which is given in each case by

$$\tan\phi = \frac{J_2}{J_1} = \frac{\delta J\omega\tau_\sigma}{J_R + J_U\omega^2\tau_\sigma^2} \tag{9}$$

and

$$\tan\phi = \frac{M_2}{M_1} = \frac{\delta M\omega\tau_\varepsilon}{M_R + M_U\omega^2\tau_\varepsilon^2} \tag{10}$$

On introducing the relaxation strength Δ, defined as

$$\Delta = \frac{\delta J}{J_U} = \frac{\delta M}{M_R} \tag{11}$$

it is easy to show that Equations 9 and 10 can be reduced (p. 40 of [3])

$$\tan\phi = \frac{\Delta}{(1+\Delta)^{1/2}}\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) = \frac{\alpha\omega\tau}{1+\omega^2\tau^2} \tag{12}$$

where

$$\alpha = \frac{\Delta}{(1+\Delta)^{1/2}} \tag{13}$$

$$\tau^2 = \tau_\sigma\tau_\varepsilon \tag{14}$$

$$\tau_\sigma = \tau(1+\Delta)^{1/2} \tag{15}$$

$$\tau = \tau_\varepsilon(1+\Delta)^{1/2} \tag{16}$$

and

$$M_R = 1/J_R \tag{17}$$

$$M_U = 1/J_U \tag{18}$$

On comparing Equations 3, 7 and 12, and taking into account Equations 15 and 16, it is easy to show that, for the case of a single relaxation time, if $\tan\phi$ is measured as a function of frequency a Debye peak will be obtained with the maximum located at the frequency $\omega_\phi^m = 1/\tau$. The maximum of the Debye peak for J_2 will be located at the frequency $\omega_{J_2}^m = 1/\tau_\sigma = 1/\tau(1+\Delta)^{1/2}$ and the maximum for M_2 will be at $\omega_{M_2}^m = 1/\tau_\varepsilon = (1+\Delta)^{1/2}/\tau$, that is, the J_2 peak will be located to the left and the M_2 peak to the right of the $\tan\phi$ peak, on the frequency scale. The separation between the peaks will increase as Δ increases. This explains, for the case of a single relaxation time, Ferry's statement (p. 47 of [4]) about the location of the three peaks in the frequency scale. Since Δ can be very large for polymers, the separation can be of several logarithmic decades in frequency. As shown in the next paragraph, a similar situation is encountered for a distribution of relaxation times. Finally, since data obtained in polystyrene will be discussed, a notation more usual in the literature for polymers will be adopted, that is [4]

$$M_1 = G' \quad M_2 = G'' \quad J_1 = J'$$

$$J_2 = J'' \quad M_U = G_g \quad M_R = G_e$$

$$J_U = J_g \quad J_R = J_e \tag{18}$$

$$\delta J = J_e - J_g \quad \delta G = G_g - G_e \tag{19}$$

and

$$\Delta = \frac{G_g - G_e}{G_e} = \frac{J_e - J_g}{J_g} \tag{20}$$

2.2. Distribution of relaxation times

For a distribution of relaxation times and an experiment performed at constant stress amplitude, J' and J'' are given, in terms of the retardation spectrum, L (p. 64 of [4]), by

$$J' = J_g + \int_{-\infty}^{+\infty}\left(\frac{L}{1+\omega^2\tau_\sigma^2}\right)\mathrm{d}(\ln\tau_\sigma) \tag{21}$$

$$J'' = \int_{-\infty}^{+\infty}\left(\frac{L\omega\tau_\sigma}{1+\omega^2\tau_\sigma^2}\right)\mathrm{d}(\ln\tau_\sigma) \tag{22}$$

and

$$\delta J = J_e - J_g = \int_{-\infty}^{+\infty} L\,\mathrm{d}(\ln\tau_\sigma) \tag{23}$$

The relaxation time is written as τ_σ to indicate that the stress amplitude is constant. If the distribution is normalized to unity, Equations 21 and 22 can be written (p. 92 of [2]) as

$$J' = J_g + \delta J\int_{-\infty}^{+\infty}\frac{\Phi\,\mathrm{d}(\ln\tau_\sigma)}{1+\omega^2\tau_\sigma^2} = J_g + \delta J F_1(x_\sigma, \gamma) \tag{24}$$

$$J'' = \delta J\int_{-\infty}^{+\infty}\left(\frac{\Phi\omega\tau_\sigma}{1+\omega^2\tau_\sigma^2}\right)\mathrm{d}(\ln\tau_\sigma) = \delta J F_2(x_\sigma, \gamma) \tag{25}$$

where

$$\int_{-\infty}^{+\infty}\Phi\,\mathrm{d}(\ln\tau_\sigma) = 1 \tag{26}$$

γ is some geometrical parameter of the distribution and

$$x_\sigma = \ln(\omega\bar{\tau}_\sigma) \tag{27}$$

where $\bar{\tau}_\sigma$ is some average relaxation time in the distribution. A similar analysis for the relaxation spectrum leads to

$$G' = G_e + \delta G F_1(x_\varepsilon, \gamma) \tag{28}$$

$$G'' = \delta G F_2(x_\varepsilon, \gamma) \tag{29}$$

$$\int_{-\infty}^{+\infty}\psi\,\mathrm{d}(\ln\tau_\varepsilon) = 1 \tag{30}$$

$$x_\varepsilon = \ln(\omega\bar{\tau}_\varepsilon) \tag{31}$$

where ψ is the normalized relaxation spectrum. The subscript ε indicates that the corresponding quantities are obtained at constant strain amplitude. Moreover, on taking into account Equation 20, the damping can be written as

$$\tan\phi = \frac{J''}{J'} = \frac{\Delta F_2(x_\sigma, \gamma)}{1 + \Delta F_1(x_\sigma, \gamma)} \tag{32}$$

and

$$\tan\phi = \frac{G''}{G'} = \frac{\Delta F_2(x_\varepsilon, \gamma)}{(1+\Delta) - \Delta F_1(x_\varepsilon, \gamma)} \tag{33}$$

It is easy to show that for the case of a single relaxation time, Equations 32 and 33 reduce to Equation 12.

The locations of the maxima of $\tan\phi$ for Equations 32 and 33 depend, in a complicated way, on Δ and on the parameters of the distribution. It can be shown [5], however, that at least for symmetrical distributions with a maximum located at the origin, Equations 32 and 33 can be written as

$$\tan \phi = \alpha F_2(x_\sigma + x_\sigma^{\mathrm{m}}, \gamma) \quad (34)$$

and

$$\tan \phi = \alpha F_2(x_\varepsilon - x_\varepsilon^{\mathrm{m}}, \gamma) \quad (35)$$

where x_σ^{m} and $x_\varepsilon^{\mathrm{m}}$ are the values for x_σ and x_ε, respectively, at which the maximum of the internal friction occurs and α is defined by Equation 13.

On comparing Equations 25 and 34, it is seen that the maximum of J'' occurs at $x_\sigma = 0$ and that for $\tan \phi$ at $x_\sigma^{\mathrm{m}} > 0$. Then, if $\tan \phi$ and J'' are measured as a function of frequency, the peak for J'' will be located to the left of the peak for $\tan \phi$. A similar analysis for Equations 35 and 29 leads to the conclusion that the G'' peak is located to the right of the $\tan \phi$ peak, when both are measured as a function of frequency. A simple comparison, as for the case of a single relaxation time, cannot be made between the different average relaxation times since x_σ^{m} and $x_\varepsilon^{\mathrm{m}}$ depend on Δ and γ in a complicated manner.

Finally, it should be pointed out that, by making a change of origin, Equations 34 and 35 can be reduced to

$$\tan \phi = \alpha F_2(\bar{x}, \gamma) \quad (36)$$

where

$$\bar{x} = \ln(\omega \bar{\tau}) \quad (37)$$

and $\bar{\tau}$ is some average relaxation time, related to $\bar{\tau}_\sigma$ or $\bar{\tau}_\varepsilon$. The maximum of $\tan \phi$ will be located at $\bar{x} = 0$.

2.3. Superposition of the tan ϕ curves

In general, α (or Δ) and τ in Equation 12 depend on temperature and on the parameters of the physical model considered. Furthermore, this equation leads to a Debye peak when $\tan \phi$ is plotted either as a function of $\omega\tau$ or as a function of ω (or f), at constant temperature. With the change of variables $x = \ln \omega$, y' $\tan \phi$, $\ln \tau = h(z)$ and $z = T$, where T is the absolute temperature, Equation 12 can be written as

$$y' = \frac{\alpha(z)}{2} \operatorname{sech}[x + h(z)] \quad (38)$$

The maxima, y'_{m}, of the y' against x (or $\tan \phi$ against $\ln \omega$ or $\ln f$) curves, determined at different values of $h(z)$ or z (or at different temperatures) are obtained for

$$x = -h(z) \quad (39)$$

with values determined by

$$y'_{\mathrm{m}} = \alpha(z)/2 \quad (40)$$

Furthermore, on dividing Equation 38 by Equation 40 leads to

$$y = y'/y'_{\mathrm{m}} = \operatorname{sech}[x + h(z)] \quad (41)$$

and the width of the peak, at half maximum, either for Equation 38 or for Equation 41, is given by

$$\Delta(\log \omega) = \Delta(\log f) = 1.144 \quad (42)$$

if z is constant.

The scaling behaviour, that is the superposition property of a family of curves in the (x, y) plane, at different $h(z)$ levels, has been studied in detail [6–8]. In particular, the family of curves described by

$$y = g[Ax + Ch(z)] \quad (43)$$

where A and C are real constants and g is a general function, lead to a scaling behaviour with a translation path parallel to the abscissa. In addition

$$\frac{\Delta[h(z)]}{\Delta x} = -\frac{C}{A} \quad (44)$$

where Δx and $\Delta[h(z)]$ are the increments in x and $h(z)$, respectively, when a point belonging to the curve for $h(z)$ is translated, by a horizontal shift, to the curve corresponding to $h(z + \Delta z)$. It is evident that Equation 41 has the form of Equation 43 with $A = C = 1$, and Equation 44 is reduced to

$$\frac{\Delta[(h(z)]}{\Delta x} = -1 \quad (45)$$

Then the y against x curves at different $h(z)$ or z levels, described by Equation 41, are related by scaling with a translation path parallel to the abscissa, which means that it is possible to construct a master curve. In addition, the increments of x and those of $h(z)$, performed during the different translations, are related by Equation 45. The considerations made are not valid, however, for the curves described by Equation 38, unless α is constant. In fact, Equation 38 is not simply a linear combination of the variables x, y' and $h(z)$ and, consequently, no scaling is present along any translation path (horizontal, vertical or at a given angle). In summary, if the relaxation process is described by Equation 12 the set of $\tan \phi$ against $\log f$ curves, at different temperatures, cannot be superposed along any translation path, unless α is independent of temperature. The normalized ($\tan \phi / \tan \phi_{\mathrm{m}}$) against $\log f$ curves, where $\tan \phi_{\mathrm{m}}$ is the maximum value of $\tan \phi$ for each curve, can then be superposed through a translation path parallel to the $\log f$ axis, that is, the time–temperature superposition is applicable and a master curve can be constructed. In addition, the increments in temperature and those of τ, performed during the different translations are related by Equation 45, that is

$$\frac{\Delta[\log \tau(T)]}{\Delta(\log f)} = -1 \quad (46)$$

It should be pointed out that all the considerations made are independent of the temperature dependence of α and τ. A more detailed analysis of the translation property of a Debye peak, including also the case where f depends on temperature, has been presented elsewhere [9]. A similar situation is encountered when a distribution of relaxation times is present, since Equations 32 and 33 have the form of Equation 43, with $h(z) = \ln \bar{\tau}_\sigma$ or $\ln \bar{\tau}_\varepsilon$ and $y = \tan \phi$, if α and γ do not depend on temperature. This means that the $\tan \phi$ against $\log f$ curves can be superposed along a translation path parallel to the $\log f$ axis. This is not the case, however, if α and γ depend on temperature. On assuming that γ does not depend on temperature, since the internal friction can be represented by Equation 36,

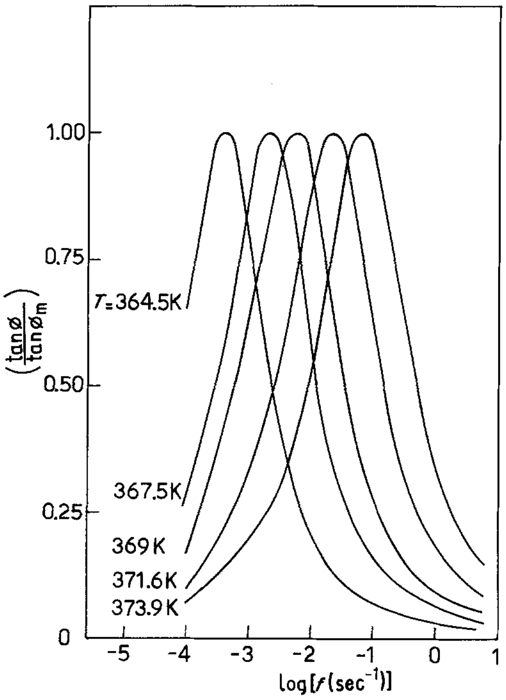

Figure 1 Normalized tan ϕ against frequency curves, at different temperatures, for atactic polystyrene. Tan ϕ_m is the maximum value of tan ϕ for each curve.

then

$$y = \frac{\tan \phi}{\tan \phi_m} = \frac{F_2(\bar{x}, \gamma)}{F_2(0, \gamma)} \qquad (47)$$

will lead to an equation similar to Equation 43 with $x = \ln \omega$ and $\ln \bar{\tau} = h(z)$. This implies that the normalized $\tan \phi$ against $\log f$ curves, measured at different temperatures, can be superposed along a translation path parallel to the $\log f$ axis, even when a distribution of relaxation times is present, if γ does not change with temperature.

Finally, it should be pointed out also that similar considerations can be made for the translation of J', J'', G' and G'' (see Equations 21, 22, 28 and 29) but in terms of the temperature dependence of δJ and δG.

3. Applications

The tan ϕ against $\log f$ curves measured at different temperatures and reported in Fig. 3a of Paper I [1] are shown here, after normalization, in Fig. 1. It is evident from the figure that they can be superposed, within experimental error, by a translation parallel to the $\log f$ axis. The master curve, obtained by translating the rest of the curves on to the one for 371.6 K, is shown in Fig. 2, where the full curve represents the data for 371.6 K and the broken curves indicate the dispersion obtained on superposing the different curves. On taking into account the experimental error, which is higher at the tails of the peaks due to a contribution of the background, it can be stated that the superposition is acceptable. The values obtained for $\Delta(\log f)$ and ΔT, during the different translations, are indicated in Table I. Moreover, observation of Figs 1 and 2 shows that the normalized peaks are symmetrical. The width of the peak at half maximum, obtained from the master curve, is

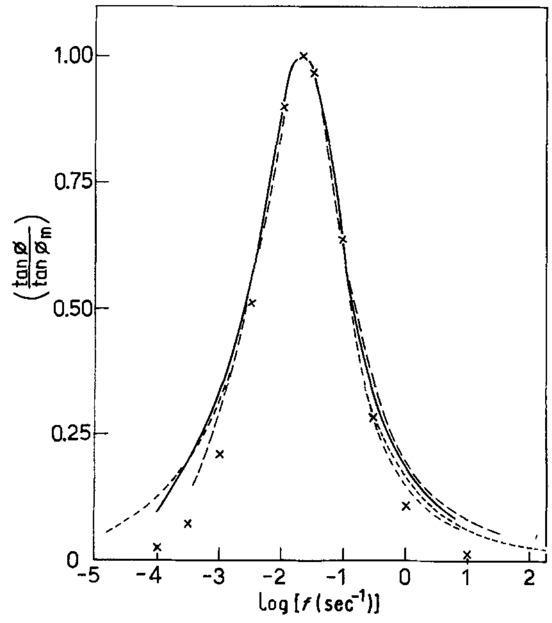

Figure 2 (——) Master curve constructed from the curves of Fig. 1 by superposing the rest of the curves on to the curve for 371.6 K; (– – –) dispersion obtained during the superposition; (x) fit to a log-normal distribution of relaxation times with $\beta = 1.6$.

$$\Delta(\log f) = 1.76 \qquad (48)$$

which is substantially larger than the value given by Equation 42. This indicates that tan ϕ is not described by Equation 12, that is, the relaxation process does not depend on a single relaxation time and a distribution of relaxation times is present. Moreover, according to Equation 46

$$\frac{\Delta[\log \bar{\tau}(T)]}{\Delta(\log f)} = -1 \qquad (49)$$

If it is assumed that the average relaxation time changes with temperature according to an Arrhenius relationship, that is

$$\bar{\tau} = \bar{\tau}_0 \exp(H/kT) \qquad (50)$$

where $\bar{\tau}_0$ is the pre-exponential factor, H is the activation enthalpy and k is Boltzmann's constant, at the reference temperature T_s the relaxation time $\bar{\tau}_s$ is

$$\bar{\tau}_s = \bar{\tau}_0 \exp(H/kT_s) \qquad (51)$$

Then

$$\ln\left(\frac{\bar{\tau}}{\bar{\tau}_s}\right) = \frac{H}{k}\left(\frac{1}{T} - \frac{1}{T_s}\right) \qquad (52)$$

TABLE I Increments of frequency and temperature during the translations performed to match the rest of the curves of Fig. 1 to the one for 371.6 K, to construct the master curve shown in Fig. 2

T (K)	$\Delta(\log f)$	ΔT (K)	$[\Delta(\log f)/\Delta(1/T)]$ (K) × 10^{-4}
373.9	−0.5	2.3	3.02
371.6	0	0	–
369	0.6	−2.6	3.16
367.5	1.0	−4.1	3.33
364.5	1.76	−7.1	3.36

which combined with Equation 40 leads to

$$\Delta(\ln f)/\Delta\left(\frac{1}{T}-\frac{1}{T_s}\right) = \Delta(\ln f)/\Delta\left(\frac{1}{T}\right) = \frac{H}{k} \tag{53}$$

Then, the ratio between the increments of $\log f$ and those of T^{-1} should be constant, if H does not depend on temperature. As shown by the last column of Table I, $\Delta(\log f)/\Delta(1/T)$ changes only slightly with temperature, with an average value

$$\Delta(\log f)/\Delta\left(\frac{1}{T}\right) = 3.22 \times 10^4\,\text{K} \tag{54}$$

leading to

$$H = 617\,\text{kJ}\,\text{mol}^{-1} \tag{55}$$

It should be pointed out that an expression similar to Equation 53 would be obtained if the relaxation time changes according to (Ch. 11 of [4])

$$\bar{\tau} = a\bar{\tau}(T_g) \tag{56}$$

where $\bar{\tau}$ is given by Equation 50 and $\bar{\tau}(T_g)$ is the relaxation time at the glass transition temperature.

On assuming that the maximum of $\tan\phi$ is at $\omega\bar{\tau} = 1$, taking for ω the value at which the maximum for $T = 371.6$ K occurs, that is, $\omega = 0.13\,\text{sec}^{-1}$, Equation 50 leads to

$$\bar{\tau}_0 = 1.6 \times 10^{-87}\,\text{sec} \tag{57}$$

when the value given by Equation 55 is used for H. It is evident that the value for $\bar{\tau}_0$ given by Equation 57 is abnormally low and H given by Equation 55 is too high, indicating that Equation 50 does not describe the temperature dependence of $\bar{\tau}$.

A relationship frequently used to describe the temperature dependence of the relaxation time in polymers ([4] (Ch. 11) and [10]) is

$$\bar{\tau} = \bar{\tau}_0 \exp\left[\frac{H_\infty}{k(T-T_0)}\right] \tag{58}$$

where H_∞ is the activation enthalpy when T tends to infinity and T_0 is an empirical constant. It can be shown easily that Equation 58 leads to

$$\ln\left(\frac{\bar{\tau}}{\bar{\tau}_s}\right) = \frac{H_\infty}{k(T_0-T_s)}\,\frac{T-T_s}{(T_s-T_0)+T-T_s}$$

$$= \Delta(\ln\bar{\tau}) = -\Delta(\ln f) \tag{59}$$

which can be written as

$$\Delta(\log f) = -C_1(T_s)\frac{T-T_s}{C_2(T_s)+T-T_s} \tag{60}$$

with

$$C_1(T_s) = \frac{H_\infty}{k(T_s-T_0)\,2.303} \tag{61}$$

and

$$C_2(T_s) = T_s - T_0 \tag{62}$$

Equation 60 is the very well known Williams–Landel–Ferry (WLF) expression [11]. Furthermore, this equation can be written as

$$\frac{-(T-T_s)}{\Delta(\log f)} = \frac{1}{C_1(T_s)}(T-T_s) + \frac{C_2(T_s)}{C_1(T_s)} \tag{63}$$

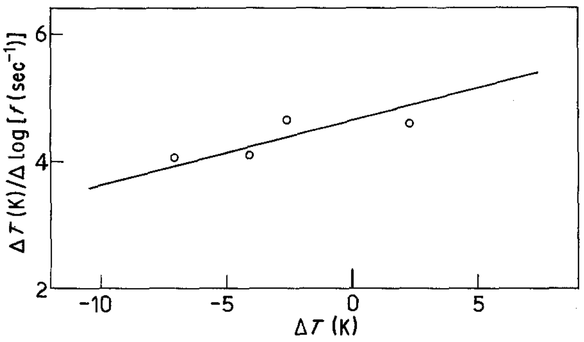

Figure 3 Plot of the data given in Table I in the way suggested by Equation 62, to obtain the parameters of the WLF equation.

A plot of $(T - T_s)/\Delta(\log f) = \Delta T/\Delta(\log f)$ against $T - T_s = \Delta T$ should then give a straight line of slope $1/C_1(T_s)$ and intercept $C_2(T_s)/C_1(T_s)$. Once C_1 and C_2 are known, H_∞ and T_0 can be determined by using Equations 61 and 62. The data of Table I are plotted in Fig. 3 in the way suggested by Equation 63. A least-squares fit to the data with $T_s = 371.6$ K leads to the straight line shown in the same figure and to the following values for the constants: $C_1 = 16$ and $C_2 = 70$ K, with a correlation coefficient of 0.97. Equations 61 and 62 then lead to $T_0 = 301.4$ K, $H_\infty/k = 2548$ K and $H_\infty = 21\,\text{kJ}\,\text{mol}^{-1}$. Furthermore, for $\omega\bar{\tau} = 1$, $\omega = 0.13\,\text{s}^{-1}$, $T = 371.6$ K and the values given previously for H_∞/k and T_0, Equation 58 leads to

$$\bar{\tau}_0 = 1.3 \times 10^{-15}\,\text{sec} \tag{64}$$

The constants of the WLF relationship, when the reference temperature is taken as T_g, are related to those of the reference temperature T_s [4, 7, 12] by

$$C_1(T_s)\,C_2(T_s) = C_1(T_g)\,C_2(T_g) \tag{65}$$

$$C_2(T_s) = C_2(T_g) - T_g + T_s \tag{66}$$

If the glass transition temperature for polystyrene is taken as 369 K, Equations 65 and 66, with the measured values for $C_1(T_s)$ and $C_2(T_s)$, lead to $C_1(T_g) = 15.2$ and $C_2(T_g) = 72.6$ K.

It is interesting to study how well the internal friction peaks can be described by some usual distribution of relaxation times. Nowick and Berry [13] have tabulated the function $F_2(\bar{x}, \beta)$ for a log-normal retardation spectrum, where β is a measure of the half-width of the distribution at the point where it falls to $1/e$ of its maximum value. Furthermore, they have given a procedure to determine the parameter β from the peak width at half maximum for J'' of $\tan\phi$ or, which is equivalent, for F_2. On using the measured value for the peak width at half maximum, as given by Equation 48, Fig. 3 of [13], which gives the dependence of the peak width at half maximum on β, and the values tabulated in [13] for $F_2(0, \beta)$, lead to

$$\beta = 1.6 \tag{67}$$

Once β is known, $\tan\phi$ can be calculated by using Equation 47 and the values for $F_2(\bar{x}, \beta)$ given in [13]. The values of $\tan\phi$ calculated in this way, for the curve at 371.6 K, are indicated by the crosses in Fig. 2. It is seen that the general behaviour of the internal friction is described fairly well by a log-normal distribution in $\bar{\tau}$. The deviation at the tails of the peak might

TABLE II $\tan \phi_m$ as obtained from the curves reported in Fig. 3a of Paper I [1] and Δ calculated with Equations 68 and 13, with $F_2(0, 1.6) = 0.36$

T (K)	$\tan \phi_m$	$\Delta \times 10^{-2}$
373.9	5.24	2.17
371.6	5.37	2.28
369	6.02	2.87
367.5	6.34	3.18
364.5	7.47	4.41

be due to a contribution of the background or to the fact that the retardation spectrum is not strictly log-normal. Moreover, according to Equation 36

$$\tan \phi_m = \alpha F_2(0, \beta) \quad (68)$$

so that α can be determined from the measured values of $\tan \phi_m$ and $F_2(0, \beta)$ tabulated in [13]. Once α is known, Δ can be calculated by using Equation 13 which, even if it is a quadratic equation, leads to a unique value of Δ with physical significance. Then, the values of $\tan \phi_m$ reported in Fig. 3a of Paper I [1] and $F_2(0, 1.6) = 0.36$ lead to the values of Δ reported in the last column of Table II, at each temperature. The measured values of $\tan \phi_m$ are also indicated in this table.

The temperature dependence of the relaxation strength of solids usually obeys a Curie–Weiss law [2], that is

$$\Delta = \frac{T_a}{T - T_c} \quad (69)$$

where T_c is some critical temperature and T_a is related to the physical model considered and to the characteristics of the specimen. Equation 69 can be rearranged as

$$\Delta T = T_a + T_c \Delta \quad (70)$$

showing that, if Equation 69 is satisfied, a plot of ΔT against Δ should be linear with slope T_c and intercept T_a. The data given in Table II are plotted in Fig. 4 in the way suggested by Equation 70, where it is evident that Equation 69 is satisfied. Moreover, a least-squares fit to the data leads to

$$T_c = 356\,\text{K} \qquad T_a = 371.5\,\text{K} \quad (71)$$

with a correlation coefficient of 0.99999.

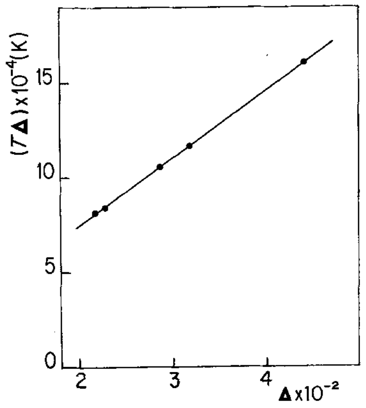

Figure 4 Plot of the parameters given in Table II, according to Equation 70, to obtain T_a and T_c.

4. Discussion

The $\tan \phi$ data have been fitted in Paper I [1] to the Vogel–Fulcher–Tanman equation

$$f = A \exp\left(\frac{B}{T - T_0}\right) \quad (72)$$

where A, B and T_0 are empirical constants related to the WLF equation, that is

$$\log\left(\frac{f(T)}{f(T_g)}\right) = -\frac{C_1(T_g)(T - T_g)}{C_2(T_g) + (T - T_g)} \quad (73)$$

where

$$B = 2.303\, C_1(T_g)\, C_2(T_g) \quad (74)$$

$$C_1(T_g) = \frac{B}{2.303\,(T_g - T_0)} \quad (75)$$

$$C_2(T_g) = T_g - T_0 \quad (76)$$

Since, according to Paper I, the $\tan \phi$ against $\log f$ curves could not be superposed to construct a master curve, Equation 72 was applied to the experimental data by using the frequency at the maximum, for each temperature, and $T_g = 369$ K, leading to $C_1(T_g) = 14$, $C_2(T_g) = 53$ K, $B = 1700$ K and $T_0 = 367.5$ K. It should be pointed out, however, that these results are incongruent since if $T_0 = 367.5$ K and $T_g = 369$ K then, according to Equation 76, $C_2(T_g) = T_g - T_0 = 1.5$ K. For consistency, $T_0 = 369 - 53 = 316$ K, which is a value closer to the one obtained from a shifting of the normalized peaks ($T_0 = 301.4$ K), that is, by using Equation 62. Fig. 5 shows a plot of $\log f_m$ against $1/(T - T_0)$, where f_m is the frequency at the maximum loss, obtained from Fig. 1, and $T_0 = 301.4$ K. A plot of $\log f_m$ against $1/T$ is also shown in Fig. 5. It can be seen that both representations are linear. Furthermore, a least-squares fit to the $\log f_m$ against $1/T$ data leads to $\bar{\tau}_0 = 2.0 \times 10^{-87}$ sec and $H = 623\,\text{kJ}\,\text{mol}^{-1}$, with a correlation coefficient of 0.998. These values are quite similar to those given by Equations 55 and 57, respectively. It was assumed in these calculations that Equation 50 holds and $2\pi f_m \bar{\tau} = 1$.

A least-squares fit to the $\log f_m$ against $1/(T - T_0)$ data, shown in Fig. 5, leads to the following values for the Vogel–Fulcher–Tanman equation (Equation 72): $A = 5.2 \times 10^{13}\,\text{sec}^{-1}$ and $B = 2490$ K, with a correlation coefficient of 0.999. Moreover, Equations 75 and 76 lead to $C_1 = 16$ and $C_2 = 68$ K, when these values are taken for A and B, and $T_g = 369$ K. On assuming that $2\pi f_m \bar{\tau} = 1$ a comparison between Equations 72 and 58 leads to $B = H_\infty / k$ and $\bar{\tau}_0 = 1/2A$ which, with the values of A and B given previously, give: $\bar{\tau}_0 = 3.1 \times 10^{-15}$ sec and $H_\infty = 20.7\,\text{kJ}\,\text{mol}^{-1}$. These values are quite similar to those obtained from a shifting of the normalized peaks. In summary, the results obtained by a shifting of the normalized internal friction curves, that is, by applying the time–temperature superposition, are nearly the same as those obtained from the position of the maxima, as indicated in Table III.

The values for $\bar{\tau}_0$ given in Table III seem reasonable when compared with the reciprocal of the Debye frequency. It should be pointed out that even if $\bar{\tau}_0$ gives the most probable value, the distribution is not very wide as indicated by the value of β given by Equation

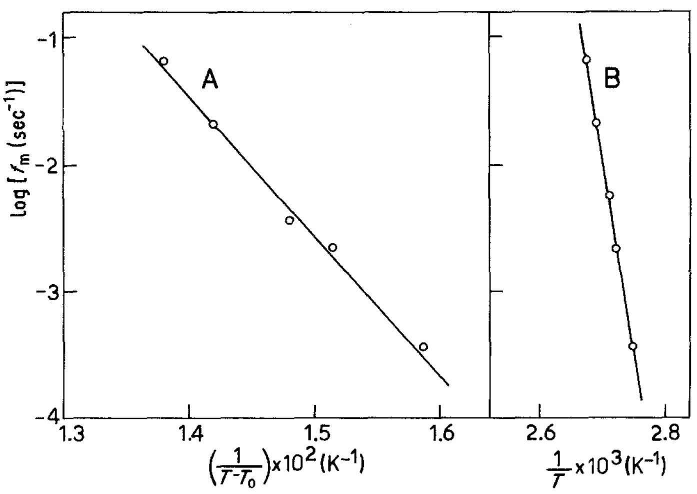

Figure 5 Plot of $\log f_m$, where f_m is the frequency at the maximum for each curve of Fig. 1, against $1/T$ (Curve B) and against $1/(T - T_0)$ (Curve A) with $T_0 = 301.4$ K.

67 and the peak width at half maximum for tan ϕ (Equation 48) compared with the one for a single relaxation time (Equation 42). Moreover, the values for H_∞, given in the same table seem also reasonable when compared with the potential energy barrier hindering the rotation of an organic compound [14].

It is interesting to make some comments on the results given by Equation 71, that is, on the parameters of the Curie–Weiss temperature dependence of the relaxation strength. Since no physical model is available, it is difficult to give a precise meaning to the parameters of Equation 69, in particular to T_a. T_c can be considered as a critical temperature below which the molecular units, which reorient under the applied stress and produce the relaxation, will reorient spontaneously even in the absence of an applied stress. It might be possible that T_c indicates the real glass transition temperature for the material. In fact, it is very well known that the value of T_g depends on the experimental technique used, that is, on the sensitivity of the method employed. It is recognized in Paper I [1] for example, that the value $T_g = 369 \pm 1$ K, as determined by means of a thermal analyser and on heating, is only approximate since the annealing effects below T_g cause the measured transition temperature to be different from the one obtained during cooling. Consequently, this may not be the material-characterizing glass transition temperature.

Finally, if an attempt is made to compare Δ and $\bar{\tau}$ as obtained from the internal friction curves with the values given by G' and G'' against $\log f$ curves, also reported in Paper I, several difficulties are encountered. The G'' curves reported in Fig. 1 of Paper I do not show well-defined maxima, as should be expected from Equation 29 if $F_2(\bar{x}_\varepsilon, \beta)$ is similar to $F_2(\bar{x}, \beta)$. Furthermore, no clear correlation can be established between $\bar{\tau}_\varepsilon$ and $\bar{\tau}$, as for the case of a single relaxation time. It should be pointed out that, with the internal friction pendulum used in Paper I, tan ϕ is measured directly [15], together with the input and output voltages. G' and G'' are calculated from these quantities. A reference voltage is generally used which means, in principle, that the measurements are performed at constant maximum stress amplitude. If this is the case, the data should be represented in terms of J' and J''. In fact, if the curves for G'' in Fig. 1 of Paper I are converted to J'' by using the expression (p. 13 of [4])

$$J'' = \frac{1}{G''[1 + (\tan\phi)^{-2}]} \tag{77}$$

no maxima are found in the frequency region considered, except for a slight bending over of the curve for 373.9 K at the lowest frequencies. All this poses the question of the meaning of the relaxation times at constant stress or at constant strain during dynamical experiments, since these two quantities are operationally well defined only for static experiments. This problem will not be discussed further, since it is beyond the purpose of this paper.

TABLE III Comparison between the values obtained for the different parameters, either from a shifting of the normalized internal friction curves (s) or from the position of the maxima in frequency (m), for $T_g = 369$ K

$C_1(T_g)$	$C_2(T_g)$ (K)	$\bar{\tau}_0$ (sec)	H_∞ (kJ mol^{-1})	T_0 (K)
15.2 (s)	72.6 (s)	1.3×10^{-15} (s)	21 (s)	301.4 (s)
16 (m)	68 (m)	3×10^{-15} (m)	20.7 (m)	–

5. Conclusions

Internal friction data on atactic polystyrene, reported recently in the literature, have been discussed. It has been shown that time–temperature superposition can be applied to the experimental curves if they are normalized properly, to account for the temperature dependence of the relaxation strength. Furthermore, the same values were obtained for some physical parameters, like the relaxation time and the activation enthalpy, from a shifting of the peaks as from the location of the maxima in frequency. The values obtained for the constants of the WLF equation are quite similar to those reported in the literature for the same material.

Finally, a general discussion on the superposition properties of the internal friction peaks was also presented.

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