

Williams–Landel–Ferry *versus* Arrhenius behaviour: polystyrene melt viscoelasticity revised

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(Received 15 November 1991; accepted 13 March 1992)

The dynamic melt viscoelasticity of polystyrene (PS) was carefully measured and critically revised for temperatures up to 290°C (about $T_g + 185^\circ\text{C}$). It has been found clearly that the Williams–Landel–Ferry (WLF) free-volume description is obeyed in the whole temperature range investigated here, whereas, rather surprisingly, no evidence was found for Arrhenius-like behaviour at the highest temperatures. The size of the PS jumping unit was quantitatively assessed to be about three skeletal bonds (i.e. one and a half monomer units). This size is large enough to cause the free volume to be the rate-limiting factor in such a wide temperature range.

(Keywords: polystyrene; melt viscoelasticity; free volume; activation energy)

INTRODUCTION

The melt viscoelasticity of polymeric materials is usually thought to be the result of two different contributions. The first is given by the molecular mobility¹: this factor is dependent on the temperature and on the local chain structure but is not believed to be a function of the whole chain structure (e.g. chain length, molecular entanglements). The other factor is independent of temperature and reflects the topological environment of the chain, giving rise to different expressions depending on whether the polymer is in the Rouse regime or in the reptational one².

In this paper attention will be focused on the first factor, namely on the effects of temperature on the viscoelastic functions. Usually these effects are modelled with two different mechanisms acting in different temperature ranges^{1,3–7}:

(i) For $T_g < T < T_g + 100^\circ\text{C}$ the kinetic bottleneck for molecular motions is the free-volume availability and the temperature effect is described by the Williams–Landel–Ferry (WLF) equation. This equation is derived directly from the assumption that the free volume is a linearly increasing function of temperature above T_g .

(ii) For $T > T_g + 100^\circ\text{C}$ the free volume is no longer considered the rate-limiting factor and the temperature dependence follows an Arrhenius-like equation. The apparent activation energy is related to the energy required for a segment to jump from an occupied site to a hole.

The well known shift factors a_T are often used to quantify the effect of temperature on the molecular relaxations. These shift factors are usually derived from the generation of master curves of the viscoelastic functions. This is accomplished, for instance, in the case of oscillatory data, by plotting:

$$G^*(\rho_0 T_0 / \rho T) \quad \text{vs.} \quad \omega a_T \quad (1a)$$

$$(\eta^* / a_T)(\rho_0 T_0 / \rho T) \quad \text{vs.} \quad \omega a_T \quad (1b)$$

$$\tan \delta \quad \text{vs.} \quad \omega a_T \quad (1c)$$

where G^* and η^* are the complex modulus and viscosity respectively and $\tan \delta$ the loss tangent. Here T_0 and ρ_0 are the material temperature in kelvins and the density in the reference state, whereas T and ρ refer to the state that has to be reduced to the reference one. Equations (1a) and (1b) apply to the real and imaginary components of the complex functions too.

In the case of WLF behaviour the shift factor is given by¹:

$$\log(a_T) = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \quad (2)$$

where the coefficients C_1^0 and C_2^0 are related to the free volume at T_0 and to the free-volume coefficient of thermal expansion.

For Arrhenius-like behaviour, a_T is given by:

$$a_T = \exp\left(\frac{E}{RT} - \frac{E}{RT_0}\right) \quad (3)$$

where R is the gas constant, E the apparent activation energy of the relaxation process and the temperature is in kelvins.

Several examples of the temperature effects on the viscoelasticity of polymer melts are reported in the literature. An Arrhenius behaviour, for instance, is reported for polyolefins^{6,7} and poly(caprolactam)⁸; whereas the WLF approach is quite general as it is applicable to a large number of materials (polymer melts and solutions, organic and inorganic glass-forming liquids) when the temperature is close to the glass transition^{1,3}. A detailed comparison between the two models is often difficult for various reasons:

(i) If the polymer can crystallize, it is practically impossible to carry out rheological measurements at temperatures between the glass transition temperature T_g and the crystallization temperature T_c .

(ii) Sometimes the transition from WLF to Arrhenius behaviour could be very smooth and with small effects, as shown by Berry and Fox⁹ for poly(dimethyl siloxane), poly(butadiene) and poly(isobutylene). In this case a precise assessment of the temperature at which the transition takes place is difficult. As underlined by Berry and Fox⁹, a close examination is needed anyway for the few cases where viscoelastic data are available in a wide temperature range.

The case of polystyrene (PS) and poly(styrene-co-acrylonitrile) (PSAN) and the corresponding rubber-modified materials is illustrative of the difficulty of an exact determination of the borderline between the two models. By means of capillary rheometer measurements, Munstedt⁷ found that these materials follow the WLF equation for temperatures up to about 250°C. With the same technique and for the same class of materials, Mendelson¹⁰ claimed that above 191°C the temperature effect is more likely described by an Arrhenius equation. Perhaps the width of the temperature range, the number of temperatures investigated and the experimental reproducibility are not yet good enough to get an unambiguous indication.

In a previous paper¹¹ it was reported, for a polycarbonate (PC) melt, that the WLF behaviour is followed up to about $T_g + 185^\circ\text{C}$. To account for this the idea was invoked that the jumping (or flowing) unit of PC is rather large, owing to many constraints on the rotational freedom of the skeletal bonds (virtual bonds less than real ones). A large jumping unit means, at least qualitatively, that the free volume plays a dominant role also at temperatures above the usually accepted borderline ($T_g + 100^\circ\text{C}$).

In this paper the case of PS is considered. The first aim is to have a detailed set of data to avoid the previously mentioned ambiguity reported in the literature between WLF and Arrhenius behaviour. Secondly in this case the number of virtual and real bonds is the same; however, some interesting free-volume effects could be expected owing to the presence of a large side-group in the chain.

EXPERIMENTAL

A narrow-distribution PS sample (supplied by Polymer Laboratories) was used. It had a peak molecular weight M_p about 570 000 and $M_w/M_n = 1.2$. A rather high molecular weight was chosen in order to be able to extend the measurements at high temperatures (with enough torque for the transducer) and to avoid low-molecular-weight tails (below the entanglement spacing), which can play the role of a solvent for the polymeric system under consideration.

Molecular-weight distributions (*MWD*) were obtained by gel permeation chromatography using tetrahydrofuran as the solvent and a Waters equipment previously calibrated with standard narrow-distribution polystyrenes.

The T_g was determined by dilatometry with a thermomechanical analyser (Perkin-Elmer series 7), which allowed in the same run the evaluation of the thermal expansion coefficient below and above T_g .

The as-received polymer powder was compression moulded at 180°C with a pressure of about 8 MPa to form discs (25 mm diameter and 1.2 mm thick), subsequently used for the viscoelastic measurements. These were carried out with a Rheometrics Mechanical Spectrometer RMS-800 operating in the oscillatory strain

mode and with parallel-plate geometry. The maximum strain amplitude used (10%) was within the linear viscoelastic limit of the material.

Dynamic measurements were preferred to those in the steady mode for several reasons:

(i) In the dynamic mode there are no problems like the distortion of the edge profile¹², which are typical of the steady measurements on polymers with the cone-and-plate or the parallel-plate geometry at deformation rates typically larger than 1 s^{-1} .

(ii) The reproducibility of the dynamic data is better than that of steady ones.

(iii) In the dynamic mode a suitable choice of the strain amplitude gives the possibility to measure the viscoelastic functions in a wide range still working in the optimum range of the torque transducer.

The rheological measurements were carried out according to the following procedure. The sample was loaded at the nominal temperature (set point) 290°C and then the first frequency sweep was run. Subsequently the temperature was lowered to 280°C and the gap between the plates was adjusted according to the thermal contraction (previously calibrated) of the steel test fixtures; then the corresponding frequency sweep was run. This procedure was repeated, with steps of 10°C, down to the minimum temperature, which was 150°C. The frequency sweep was from 0.1 to 100 rad s^{-1} at all the temperatures. The differences between the set point and the actual temperatures are reported in Table 1. In what follows we shall refer to the nominal temperatures, whereas all the calculations were made with the actual ones.

As reported previously¹¹ the experimental procedure described above was preferred to that of using a new sample for each temperature: preliminary investigations revealed that this other method has intrinsically a larger experimental error (due perhaps to the non-reproducibility of loading the sample, differences in the edge profiles of the material between the plates, etc.).

The procedure actually followed has the drawback of

Table 1 WLF parameters and apparent activation energies as derived from the a_T factors obtained by $\tan \delta$ superposition. C_1^0 and C_2^0 refer to the case $T_0 =$ reference temperature. C_1^\ddagger and C_2^\ddagger are calculated from the corresponding C_1^0 and C_2^0 with the use of equations (4a) and (4b). Apparent activation energies are derived from equation (3) (see also the text)

T_0 , set pt (°C)	T_0 , actual (°C)	C_1^0	C_2^0	C_1^\ddagger	C_2^\ddagger	E_a (kJ mol ⁻¹)
150	150.3	6.70	91.34	13.29	46.04	
160	160.5	6.02	100.57	13.42	45.09	214.5 ± 8.6
170	170.6	5.49	111.46	13.35	45.86	185.5 ± 8.1
180	180.7	5.10	123.38	13.21	47.68	167.8 ± 1.9
190	190.5	4.55	128.68	13.57	43.18	149.4 ± 8.8
200	200.4	4.31	140.66	13.38	45.26	129.3 ± 2.6
210	210.4	4.03	150.91	13.36	45.51	120.1 ± 2.7
220	220.4	3.76	160.41	13.41	45.01	110.2 ± 3.1
230	230.4	3.55	170.58	13.39	45.17	101.8 ± 1.7
240	240.4	3.35	180.46	13.42	45.06	95.3 ± 2.0
250	250.5	3.19	191.00	13.39	45.50	89.2 ± 1.5
260	260.6	3.06	201.89	13.34	46.29	80.7 ± 3.5
270	270.6	2.88	211.20	13.36	45.50	72.5 ± 1.2
280	280.6	2.71	220.01	13.44	44.41	69.1 ± 0.7
290	290.6	2.57	229.31	13.50	43.71	
			Average	13.39	45.28	
				±0.08	±1.02	

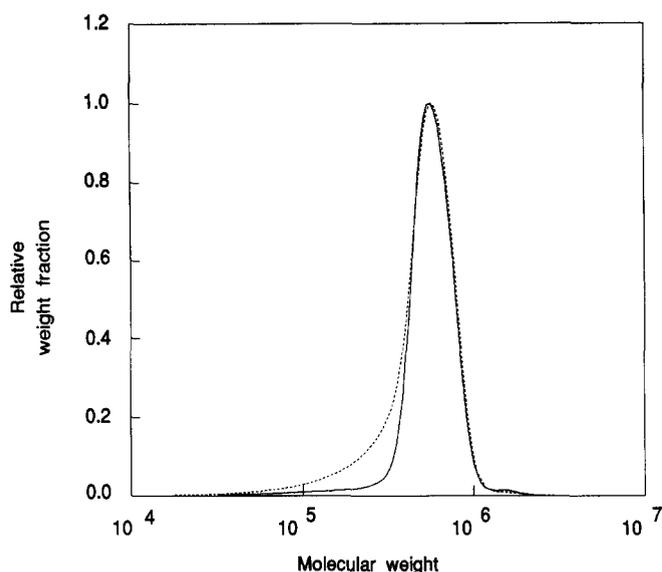


Figure 1 Molecular-weight distribution of the PS investigated before (full curve) and after (dotted curve) the rheological measurements

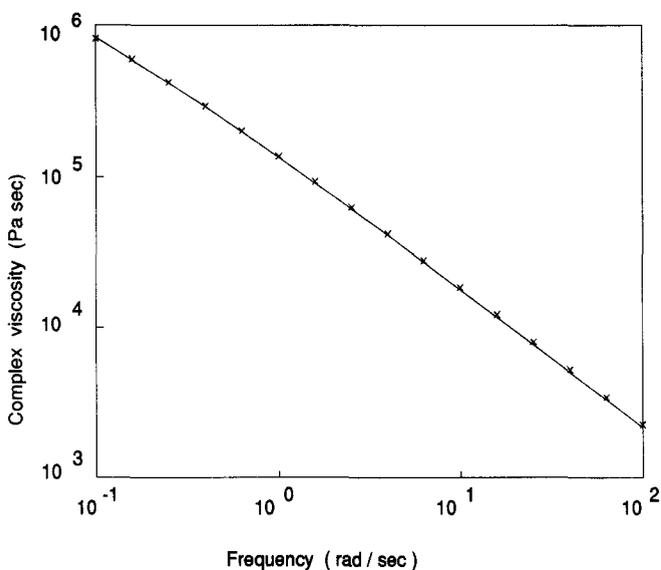


Figure 2 Complex viscosity versus frequency at 180°C: fresh sample (crosses) as compared with the procedure described in the text (full curve)

a long residence time of the sample within the environmental chamber; however, this effect can be considered of minor importance.

In *Figure 1* the *MWDs* of the material before and after the rheological measurements are plotted. It can be observed that the peak molecular weight is unchanged and that there is an increase of the contribution of lower molecular weights due to some material degradation. However, this tail in the distribution proved to have a very minor effect. *Figure 2* shows the complex viscosity at 180°C as obtained with this procedure (after about 3 h residence time in the environmental chamber of the rheometer) and is compared with the data obtained with a fresh sample. The differences (5% or less) are consistent with the typical reproducibility of rheological data. In the appendix further support is given about the weak relevance of *MWD* changes for the purposes of this work.

RESULTS

Thermal properties

From the dilatometry experiments both the T_g and the thermal expansion coefficients were evaluated.

The T_g value, as expected, depends somewhat on the experimental conditions (heating and cooling rates). Its exact value is not very critical for the discussion of the rheological data; however, a typical value of 105°C was extracted as the average of several temperature scans. This value is consistent with the most recent literature data collection¹³.

As the volume thermal expansion coefficients, the following data were obtained:

$$\alpha_g = (1.73 \pm 0.38) \times 10^{-4} \text{ (}^\circ\text{C}^{-1}) \quad \text{for } T < T_g$$

$$\alpha_1 = (10.29 \pm 0.57) \times 10^{-4} \text{ (}^\circ\text{C}^{-1}) \quad \text{for } T > T_g$$

Rheological data analysis

Starting from the temperature–frequency superposition principle, the viscoelastic quantities were reduced to master curves by means of suitable software (Rhecurve, supplied by Rheometrics Inc.). This software outputs the shift factors a_T , which give the best superposition, without making any assumption on the functional dependence on temperature of the shift factors themselves. The procedure was applied, independently, to the following functions: G' , G'' , $\tan \delta$ and η^* .

As an example, *Figure 3* shows the master curves, reduced at 190°C, of the four functions mentioned above.

For the moduli G' and G'' and the complex viscosity η^* the shift factors were computed both with and without the vertical shift correction due to the density–temperature factor (equations (1a) and (1b)). The a_T thus obtained were fitted to the WLF equation by means of a non-linear least-squares analysis (Nelder–Meade simplex algorithm).

The results of the WLF fits are extensively reported in *Table 1* for the case of a_T derived from the generation of $\tan \delta$ master curves. The WLF constants obtained are shown for each possible reference temperature. As pointed out by Prest and Porter¹⁴ the WLF parameters are rather sensitive to experimental error scatter and its consequences on the shift factors. To check the reliability, each (C_1^0, C_2^0) pair was transformed to T_g as the reference temperature through the equations:

$$C_2^g = C_2^0 - T_0 + T_g \quad (4a)$$

$$C_1^g = \frac{C_1^0 C_2^0}{C_2^0 - T_0 + T_g} \quad (4b)$$

In *Table 1* the T_g -referenced WLF constants are also shown, and it can be seen that they are quite consistent over the whole temperature range, namely up to about $T_g + 185^\circ\text{C}$. *Figure 4* shows the WLF fit of the shift factors obtained from $\tan \delta$ superposition with 190°C as the reference temperature.

On the other hand to check the Arrhenius equation the apparent activation energy E_a was also calculated by making linear regressions of $\ln(a_T)$ vs. $(1/T)$ where T is the absolute temperature. For each reference temperature T_0 the regressions were performed in the range between $T_0 - 10^\circ\text{C}$ and $T_0 + 10^\circ\text{C}$. To increase the number of data points the regressions were also computed in the range between $T_0 - 20^\circ\text{C}$ and $T_0 + 20^\circ\text{C}$, and the results were practically equal to those obtained with the smaller temperature range.

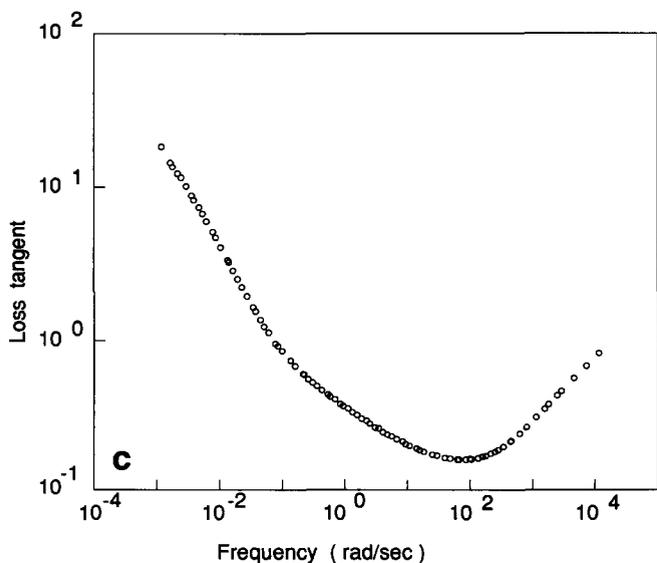
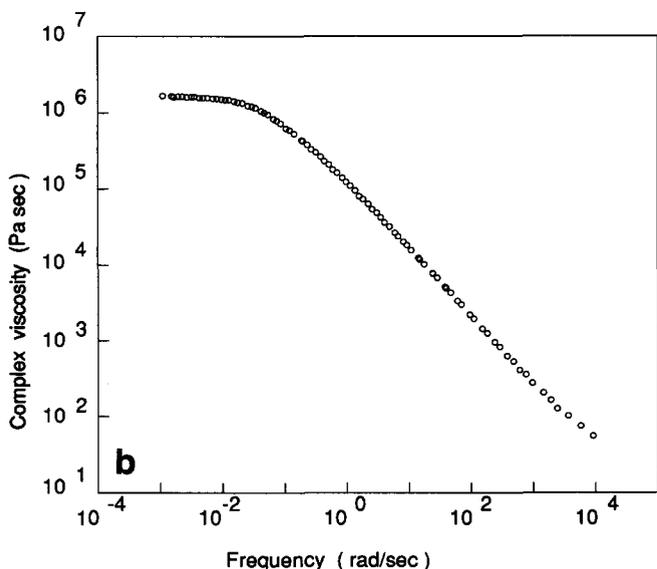
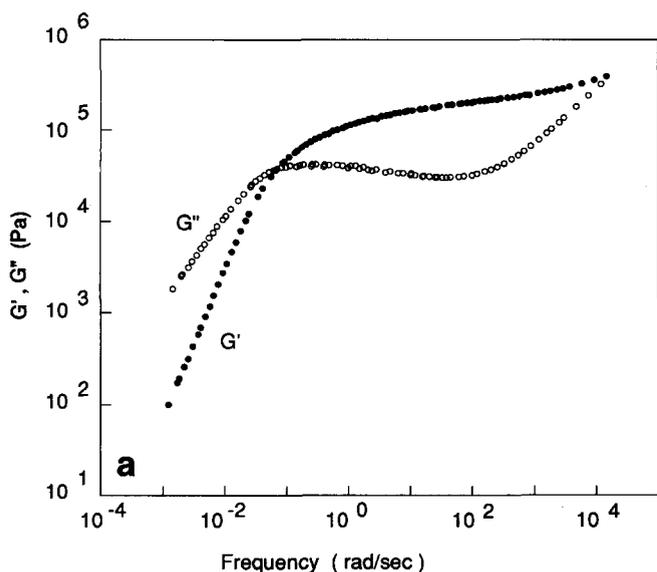


Figure 3 Master curves at 190°C of various viscoelastic functions: (a) storage and loss moduli, (b) complex viscosity, (c) loss tangent

The activation energies E_a thus obtained are reported in Table 1 together with their standard deviation. It is evident that a constant activation energy is not reached in the temperature range investigated. Furthermore the tendency to an asymptotic behaviour of E_a for high temperatures can be successfully accounted for within the WLF framework. In fact E_a being defined as:

$$E_a = R \frac{d \ln(a_T)}{d(1/T)} \quad (5)$$

it follows that for the WLF behaviour E_a is given by:

$$E_a = \frac{2.303RC_1^*C_2^*T^2}{(C_2^* + T - T_g)^2} \quad (6)$$

Figure 5 shows the plot of equation (6) (resulting from the average values for C_1^* and C_2^*) and the experimental values obtained for E_a . It can be observed that equation

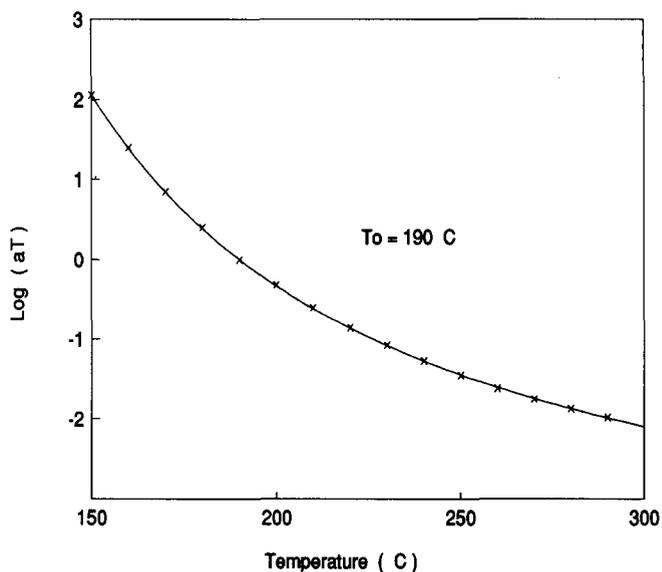


Figure 4 Shift factors (crosses) derived from loss tangent superposition and WLF fit (full curve)

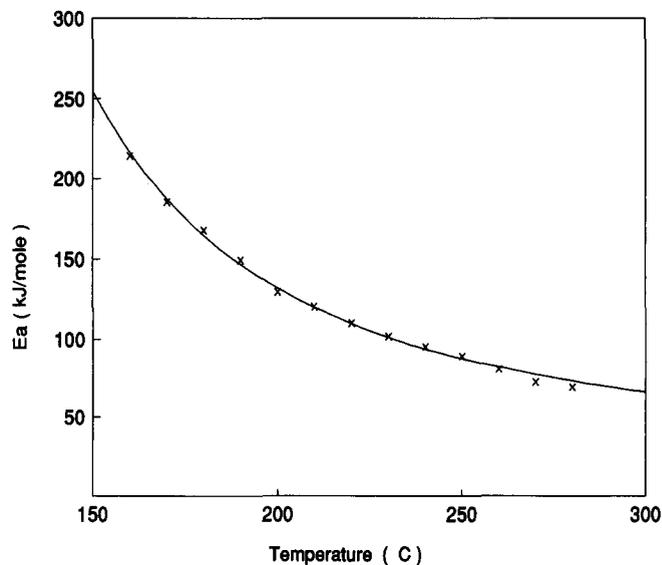


Figure 5 Activation energies (crosses) estimated from the experimental shift factors and with the use of equation (5). The full curve is the WLF prediction (equation (6))

Table 2 WLF constants and free-volume parameters (T_g -referenced) as calculated from the shift factors obtained from the master curve construction of different viscoelastic functions

Viscoelastic function	C_1^g	C_2^g	f_g/B	α_f/B ($10^{-4}^\circ\text{C}^{-1}$)
$\tan \delta$	13.39 ± 0.08	45.28 ± 1.02	0.0324	7.16
G'	12.72 ± 0.13	45.57 ± 1.42	0.0341	7.49
G''	14.00 ± 0.77	43.16 ± 5.42	0.0310	7.19
η^*	12.58 ± 0.22	45.65 ± 2.64	0.0345	7.56
G'^a	14.62 ± 0.15	36.84 ± 0.87	0.0297	8.06
G''^a	13.55 ± 0.33	40.39 ± 2.50	0.0320	7.93
η^{*a}	13.27 ± 0.39	46.73 ± 4.60	0.0327	7.00
Average values	13.44 ± 0.65	43.77 ± 3.3	0.0327 ± 0.0015	7.48 ± 0.37

^aVertical shifting due to density-temperature correction was applied

(6), which has no adjustable parameters, reproduces very well the behaviour of E_a in the whole temperature range.

The same analysis reported above for $\tan \delta$ was carried out for the other viscoelastic functions. The average WLF parameters (T_g -referenced) thus obtained are listed in Table 2. It is remarkable that the values are consistent with each other. Some minor differences can be ascribed to the fact that the precise a_T values can depend somewhat on the shape of the viscoelastic function under consideration and on the numerical range it spans.

The largest differences are found for the cases of G' and G'' with the density-temperature vertical shift correction. Two comments should be emphasized about this point. The first is that the various WLF curves derived with the coefficients of Table 2 differ only close to T_g , whereas in the experimental temperature range they show very small differences. The second is that the density-temperature correction given in equations (1a) and (1b) could be too strong. A possible weaker correction was first proposed theoretically by Graessley and Edwards¹⁵, who used scaling arguments. Quite recently, a detailed investigation on poly(isobutylene) melts seemed to give experimental support to this idea¹⁶. However, a detailed discussion about the exact formula of the vertical shift factor is beyond the scope of this paper.

The Arrhenius analysis on the a_T derived from the moduli and the viscosity gave indications very similar to those found for the $\tan \delta$ case (Figure 5 and Table 2).

The free-volume parameters are simply related to the WLF constants

$$f_g = \frac{B}{2.303C_1^g} \quad (7a)$$

$$\alpha_f = \frac{B}{2.303C_1^g C_2^g} \quad (7b)$$

where B is a constant, f_g is the fractional free volume at T_g and α_f is the free-volume thermal expansion coefficient. The parameters obtained with the WLF analysis on the different viscoelastic quantities are also shown in Table 2 and again good consistency is found.

The constant B is of the order of unity and its precise determination requires a further assumption. One possibility is to assume:

$$\alpha_f = \alpha_l - \alpha_g \quad (8)$$

which gives B values of the order of 0.9 ± 0.3 for many polymers¹.

In our case, considering the mean α_f/B value from Table 2 and the experimental α_l and α_g , we get $B = 1.16$ within the typical range reported by Ferry.

Before concluding this section we should mention a further, more severe, test of the validity of the WLF equation in the temperature range up to $T_g + 185^\circ\text{C}$ at least. The a_T for temperatures ranging from 210 to 290°C were considered separately. This range is above $T_g + 100^\circ\text{C}$ where commonly Arrhenius behaviour is expected. By taking the shift factors from $\tan \delta$ master curves, the following WLF mean parameters were obtained

$$C_1^g = 13.69 \pm 0.9$$

$$C_2^g = 44.26 \pm 4.78$$

These values are very similar with those obtained by using the data at all the temperatures (Table 1). Only the deviations around the mean values are somewhat larger due to the restricted data set. Thus we have another indication that the WLF analysis is the correct one for all the temperatures investigated here.

DISCUSSION

As reported for the case of polycarbonate¹¹ there are many convincing indications that the WLF free-volume model is better than the Arrhenius one for the interpretation of viscoelastic data up to temperatures around $T_g + 185^\circ\text{C}$, a temperature range significantly larger than usually reported.

The free-volume concept is physically plausible and simple. Furthermore, it is quite universal as it applies to any kind of amorphous material¹⁷, like organic, inorganic, polymeric and metallic ones. However, the versatility of the free-volume concept is paradoxically a reason for its ambiguity. As recently pointed out¹⁸, perhaps the most difficult point is to have an unambiguous criterion to define, geometrically, the regions of occupied and unoccupied space.

From the classical analysis of Cohen and Turnbull¹⁹ on molecular transport in liquids, it is well known that the limiting factor controlling diffusion or fluidity is the probability $P(v^*)$ of finding a hole with volume exceeding some critical value v^* . This probability is given by a Doolittle-like equation:

$$P(v^*) = \exp(\gamma v^*/v_f) \quad (9)$$

where γ is a numerical factor and v_f is the average free volume per jumping (or diffusing) unit.

The critical free volume v^* should be related to the typical size of a molecule of the liquid. The effect of temperature, in this framework, is to increase v_f , and when v_f is much larger than v^* the probability $P(v^*)$ tends to 1 and the free volume is no more the rate-limiting factor.

In the case of liquids formed of simple molecules equal to each other, it is quite natural and reasonable to choose a molecule as the jumping unit. However, for chain molecules, the definition of the segmental unit could be more ambiguous.

In the case of PC¹¹ it was qualitatively argued that the jumping unit should be rather large because of the fact that many real bonds have no rotational freedom (virtual bonds less than real ones²⁰). Thus a large

jumping unit makes the free volume to be the rate-limiting factor for molecular relaxations in a wide temperature range.

The case of PS could be more intriguing as it shows analogies and differences with respect to the PC case. The difference is that here we have the number of real backbone bonds equal to that of virtual backbone bonds²⁰. The analogy is that also in PS there is the presence of a bulky group, namely the phenyl side-group. Thus the problem arises of assessing, in some way, the size of the jumping unit in the PS chain.

As the macromolecular dynamics is essentially the dynamics of conformations, two limiting cases can be considered as borderlines for this problem:

(i) In a vinyl chain each bond has some conformational freedom. In this framework each chain segment can be thought to represent a jumping unit, whose size should then be the typical mean molecular volume associated to a single chain bond.

(ii) The equivalent Kuhn freely jointed chain can also be considered, where each bond of actual length l_0 is replaced by an equivalent one of length $l = C_\infty l_0$, C_∞ being the characteristic ratio. The value of this quantity is approximately 10 for PS²¹, this leading to the idea that the jumping unit should consist of 10 skeletal bonds (that is, five monomers).

It is intuitive that both these pictures are very crude and they are not expected to be correct. In case (i) the jumping unit size is probably underestimated. The freedom of each bond is quite limited: purely C–C bond chains have only three possible conformers (*trans*, *gauche* +, *gauche* –) for each skeletal bond. Secondly, a severe steric hindrance effect is introduced by the presence of the phenyl ring side-group. On the other hand case (ii) has the opposite limitation (jumping unit size overestimation) because each Kuhn segment has full orientational freedom with respect to the others. It seems reasonable that a chain segment to be considered as a jumping unit should have a conformational freedom intermediate between case (i) and case (ii).

The following physical picture can be conceived: let us imagine a jumping unit as an isolated 'solvent' molecule moving in the field originated by the surroundings. This idea could be rather speculative; however, it can be considered as a definition: the jumping unit is taken to be a portion of the chain which moves independently as if it were a 'solvent' molecule. Of course, in this mean-field approach, the test jumping unit is 'solvent-like' whereas the surroundings are still polymeric. Thus the situation becomes quite similar to that of diffusion in polymer–solvent systems when the solvent concentration is infinitely small.

For this problem a free-volume-based model was proposed by Vrentas and Duda²². They derived the following expression for the apparent activation energy E_D for the diffusion process of the solvent molecule:

$$E_D = A \frac{RT}{(K_{22} + T - T_{gp})^2} \quad (10)$$

where R is the gas constant, T the absolute temperature, T_{gp} the glass transition temperature of the pure polymer and K_{22} a parameter that can be identified with the C_2^2 of the pure polymer. The constant A contains the contribution of several other parameters and has

the dimensions of temperature. Interestingly Vrentas and Duda found a linear relationship between A and the molar volume at 0 K of the solvent. As a consequence E_D becomes practically temperature-independent (Arrhenius-like) for temperatures rather close to T_g when the solvent molecule is small. Conversely large solvent sizes show E_D values that are temperature-dependent in a wider range.

With the above-mentioned assumptions A should give an estimate, in this case, of the molar volume of the chain jumping unit. For this purpose the activation energies of *Table 1* were fitted to equation (10). A least-squares fit gave $A = 1399$ K and the fit is virtually indistinguishable from that of *Figure 5*. The differences between the WLF fit and the Vrentas–Duda one are less than 0.2%.

The A value of 1399 K means (see figure 5 of ref. 22) an approximate 0 K molar volume of $140 \text{ cm}^3 \text{ g}^{-1} \text{ mol}^{-1}$. As the molar volume at 0 K of the PS repeat unit is $94 \text{ cm}^3 \text{ g}^{-1} \text{ mol}^{-1}$ it follows that the jumping unit is about one and a half monomer units, i.e. three skeletal bonds. This indication is consistent with the previous qualitative indication that the jumping unit size should be between one and ten bonds.

In the scheme proposed here a constant activation energy is reached only asymptotically at high temperatures. Equation (10), together with the A value obtained, shows for instance that at 300°C an increase of 10°C results in a still significant activation energy decrease (about 5%).

It is possible to conclude that the WLF free-volume approach holds, for PS, up to $T_g + 185^\circ\text{C}$ at least. This seems to be due to the rather large size of the jumping unit.

ACKNOWLEDGEMENTS

The author is indebted to Dr Ravanetti for the thermal measurements and to Dr Castellani for a critical reading of the paper.

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APPENDIX

After running the experiments there was an increase in the low-molecular-weight tail (*Figure 1*). This tail, if

effective, should give rise for instance to a decrease of the complex viscosity. This decrease, in the experimental procedure followed, is expected to be more pronounced at low temperatures, which correspond to longer residence times. Thus the net apparent result is a reduced effect of temperature on the viscoelastic quantities. Should this apparent effect be strong then it will change the data more likely towards the Arrhenius behaviour, which is the opposite of what is actually found.