Molecular interpretation of T_{ll}, the rubbery–viscous 'transition' temperature of amorphous polymers

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Many physical and mechanical properties of amorphous polymers show anomalous behaviour at a temperature above T_g, designated T_{ll}, the 'liquid–liquid transition temperature'. It is suggested here that T_{ll} can be considered to be the rubbery–viscous 'transition' temperature of amorphous polymers, analogous to T_g, the glassy–rubbery transition temperature. At T_{ll}, the viscous dissipation goes through a maximum due to a shift in response of the molecules to stress from a coiling–uncoiling process (elastic rubbery region) to slippage between the molecules (viscous region). It is argued here that this maximum is responsible for the occurrence of a maximum in log(decrement) traces obtained by torsional braid analysis (t.b.a.) above T_g.

INTRODUCTION

There is considerable evidence of anomalous behaviour in the properties of atactic polystyrene (PS) at ~180°C; this is above the glass transition temperature ($T_g \approx 100$°C), and suggests some sort of additional 'transition'. This temperature has been called the liquid–liquid transition temperature[1], T_{ll}.

Spencer and Dillon[2] reported a break in slope in the plot of ln η_0 *versus* $1/T$ around 190°C, where η_0 zero shear viscosity. In 1950 Fox and Flory[3] reported a second-order transition around 160°C because they noticed a break at this temperature in the slope of the relationship between specific volume V and T. However, in 1971 Flory *et al.*[4] reported only a discontinuity in the coefficient of expansion α at around 160°C, rather than a break, which suggested to them a third-order transition.

The existence of a T_{ll} 'transition' has also been detected using new experimental techniques. Most recently the elastic properties of polymer melts have been measured by Maxwell and Nguyen[5], who reported that 'polystyrene melts exhibit abrupt changes or 'transitions' as a function of temperature in the following properties: (a) yield stress, (b) steady state stress, (c) time for a strain recovery process to be finished, (d) magnitude of the initial recovery.' LaCabanne *et al.*[6] have shown the existence of two current maxima by the method of thermally stimulated current (t.s.c.) for anionic PS; one peak occurs at T_g, and the other at 170°C. Evidence for the existence of T_{ll} has also been reported using other techniques, including X-ray[7,8], Fourier transform infra-red spectrometry[9], spin-probe techniques[10], diffusion and solubility measurements[11], the mechanical spectrometer[12], and the Rheovibron with and without use of a support[13]. T_{ll} has also been postulated for other amorphous polymers, such as polybutadiene[14] and poly(methyl methacrylate)[12,15].

However, by far most of the evidence in support of T_{ll} as a transition with a molecular origin has been obtained from torsional braid analysis (t.b.a.)[16,17]. Some of the important results found by t.b.a. are[16–20]:

(1) T_{ll}, like T_g, varies linearly with the inverse number-average molecular weight, $\bar{M}_n$. For homopolymers at M_c (the critical molecular weight for entanglement) the line changes its slope abruptly, as shown in *Figure 1*; when experiments on binary blends are performed, the T_{ll} transition of the individual components are observed if one component has $M_n < M_c$ and the other $M_n > M_c$;

(2) for M_n below M_c, $T_{ll}/T_g \approx 1.2$;

(3) the effects of plasticizer on T_{ll} and T_g are similar.

The existence of a transition at T_{ll} has been challenged by several workers. Patterson, Bair, and Tonelli[21] have stated that T_{ll} as measured by t.b.a. is a 'reflection of the temperature at which the sample flows under the influence of gravity' and have concluded that T_{ll} is just a kinetic phenomenon without any thermodynamic basis. Nielsen[22] has argued that in t.b.a. one should expect to get a peak in log (decrement, Δ) above T_g, not because of any molecular transition but due to interference of the braid in

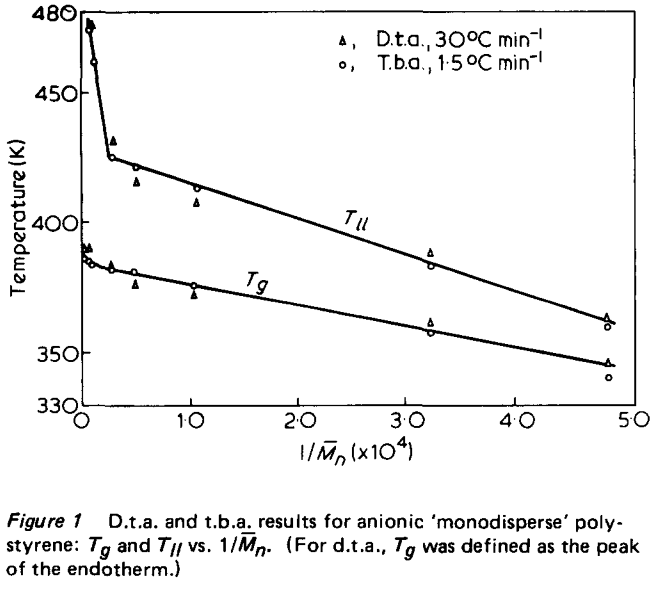

Figure 1 D.t.a. and t.b.a. results for anionic 'monodisperse' polystyrene: T_g and T_{ll} vs. $1/\bar{M}_n$. (For d.t.a., T_g was defined as the peak of the endotherm.)

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the composite and decreasing viscosity of the polymer as the temperature increases. Thus, he has referred to T_{ll}, which is the temperature where the peak in Δ occurs, as an artifact of the t.b.a. technique, and he attributes the molecular weight dependence of T_{ll} to the strong dependence of polymer viscosity on molecular weight. Neumann *et al.*[23], in a more quantitative argument, have supported Nielsen, calling T_{ll} an artifact.

In the following sections it will be argued that the available experimental information favours the hypothesis that T_{ll} is a transition with a molecular origin. A possible molecular mechanism for the T_{ll} transition is then discussed. However, before the argument in support of T_{ll} as a transition is given, it seems appropriate here to define the term 'transition'. The author defines 'transition' as a shift in response of the polymer molecules to an external force within a sufficiently narrow range of temperature (or time) to be considered important in the study, processing, or application of the polymer. This definition is, of course, subjective since it is not specified what is meant by 'sufficiently narrow range of temperature' or what can be considered 'important'. However, it is clear that T_g satisfied this definition well; and as will be shown, around a temperature called T_{ll} the response of the amorphous polymer molecules shifts from coiling-uncoiling (rubbery region) to slippage between the molecules (viscous region) within a small temperature range which can be measured by such techniques as t.b.a. The author believes that this 'transition' can be of considerable importance, for example in processing the polymer melt, since the swelling of the extruded polymer could be significantly different depending on whether the process temperature is below or above T_{ll}.

EVIDENCE FOR T_{ll} AS A TRANSITION

The following experimental information suggests that T_{ll} has a molecular origin and is not an artifact.

(1) the existence of a transition identified as T_{ll} has been reported by many workers based on various techniques as described in the Introduction. It is highly improbable that an artifact which suggests itself as a transition should occur in t.b.a. results around the same temperature at which these other techniques have shown indications of a transition.

(2) For homopolymers, T_{ll}, like T_g, is a linear function of $(M_n)^{-1}$ with a change in slope at M_c[16,17,20]. Furthermore, experiments on binary blends[24] and copolymers[25] have given strong support to the belief that T_{ll}, like T_g, corresponds to an isofree volume state.

(3) The transition at T_{ll} does not correspond to an isoviscous state[24,25]. Nielsen[22] has attributed the increase in T_{ll} with molecular weight to the strong dependence of the polymer viscosity on molecular weight. By extending Nielsen's argument further, as Neumann *et al.*[23] have done, it can be shown that if T_{ll} were an artifact it should occur at an isoviscous state. Work on blends of monodisperse polymers[24] and also on copolymers[25] has shown that the T_{ll} transition corresponds to an isofree volume but not an isoviscous state.

(4) The ratio T_{ll}/T_g has been found to be approximately equal to 1.2 for $M_n < M_c$ which suggests that T_{ll} has a molecular origin as does T_g.

(5) If T_{ll} were an artifact as Nielsen[22] has proposed, then no other peaks in Δ above T_{ll} should be observed. However, some polymers exhibit another peak in Δ above T_{ll} at a temperature called T_{ll}'[17,19,26]. It may just be that Nielsen's argument applies to T_{ll}' rather than to T_{ll}.

Senich and MacKnight[27], using dynamic spring analysis (d.s.a.), observed an apparent relaxation above T_g for polystyrene, which they attributed to solvent evolution from the polymer–spring composite because it was found to be irreversible. This apparent relaxation cannot be the same as T_{ll}, since T_{ll} is found to be reversible even after the temperature is raised much above the boiling temperature of the solvent[20].

Patterson *et al.*[21] have stated that T_{ll} as measured by t.b.a. has no thermodynamic basis and is only 'a reflection of the temperature at which the sample flows under the influence of gravity'. They predicted that 'for samples with molecular weights above the critical molecular weight for chain entanglement, no peaks above T_g in d.s.c. or t.b.a. traces would be expected'. Experimental results[20] such as the linear relationship between T_{ll} and $(M_n)^{-1}$ show evidence for T_{ll} when $M_n > M_c$. In addition, the viscosity of polystyrene homopolymers at their T_{ll} temperature has been found[20] to be approximately 10^4–10^5 poise, which is 10^6–10^7 times larger than the viscosity of water at room temperature. It is unlikely that a polymer with such a high viscosity would show any significant flow under the influence of gravity between the closely packed fibres of the braid. Since T_{ll} is found to be reversible and occurs at a constant temperature, the possibility of this flow is further reduced. However, if such flow does occur, there is still no clear reason why it should manifest itself as a peak in t.b.a. log (decrement, Δ) traces. Boyer *et al.*[11] have strongly criticized Patterson *et al.*[21] on other points.

MOLECULAR ORIGIN OF T_{ll}

The typical change in modulus of an amorphous polymer with temperature is shown in *Figure 2*. Below T_{g1}, the temperature dependence reflects the response of the molecules to an external force by means of localized motion involving a few atoms (4 or 5) along the backbone chain[28]. As more free volume becomes available to the

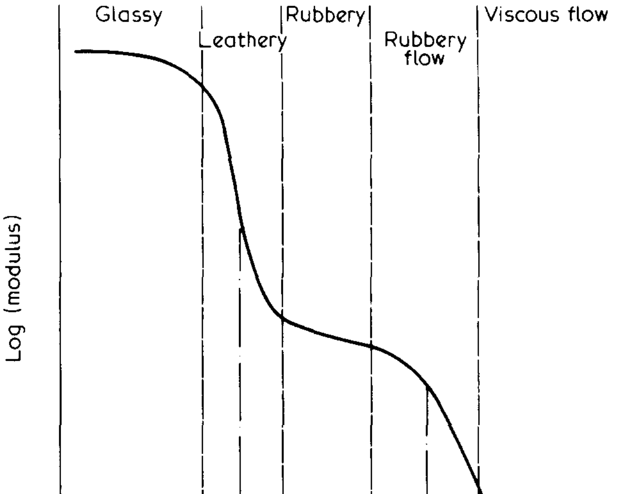

Figure 2 Five regions of viscoelastic behaviour of amorphous polymers. The leathery and rubbery flow transition regions separate the glassy, rubbery, and viscous flow regions from each other

molecules, at a temperature called T_g, the major response of the molecules shifts to a coiling–uncoiling process[28]. This transition (T_g) occurs in the leathery region ($T_{g1} < T < T_{g2}$) which separates the glassy region ($T < T_{g1}$) from the rubbery region ($T_{g2} < T < T_{r1}$).

Between T_{g2} and T_{r1} the polymer behaves as an elastic rubber with negligible viscous dissipation. It is important to remember that at least two conditions must be satisfied by the molecules before the polymer can act as a rubber: (1) the molecules must have the ability to return to their original configuration and position after they are stretched and released; this condition is satisfied since the random-coil configuration represents a state of high entropy; (2) there must exist some binding between the molecules to hinder their slippage past one another; this is satisfied by the secondary cohesive forces between the molecules and also by mechanical entanglement of the chains when $M_n > M_c$.

At T_{r1} the polymer begins to acquire viscous flow characteristics, and at a higher temperature designated T_{r2} (see *Figure 2*) the polymer may be characterized mainly as a viscous fluid. It is proposed here that due to breakage of the bonds between the molecules the major response of the molecules shifts from a coiling–uncoiling process to slippage between the molecules at the T_{ll} transition temperature. This transition occurs in a region which can be referred to as the rubbery flow region ($T_{r1} < T < T_{r2}$) which separates the rubbery region ($T_{g2} < T < T_{r1}$) from the viscous flow region ($T > T_{r2}$).

Therefore, T_{ll} is defined here as the temperature at which the bonds between the molecules are broken. It will be assumed that there exist two kinds of bonds between the molecules: (1) secondary cohesive forces such as hydrogen bonds; and (2) mechanical entanglements which would exist only if $M_n > M_c$. We can discuss different ways of breaking these bonds. One way would be to increase the free volume to cause excess distance between the molecules. This is accomplished with the t.b.a. technique by increasing the temperature. If T_{ll}, like T_g, is a free volume phenomenon, we should expect it to correlate with $\bar{M}_n$ rather than $\bar{M}_w$, since each molecule introduces approximately the same amount of free volume, regardless of its weight. The experimental results support this hypothesis, since T_{ll} is found to be a linear function of $(\bar{M}_n)^{-1}$ with a break in slope at M_c (see *Figure 1*). The break at M_c can be understood by resolving the experimental curve in the M_c region into its contributing components, as is shown in *Figure 3*. For $\bar{M}_n < M_c$ the molecules would slip past one another if enough free volume existed to overcome their intermolecular cohesive forces. For $\bar{M}_n > M_c$, an *extra* amount of free volume is needed to overcome chain entanglements. For binary blends where one of the components has $M_n < M_c$ and the other $M_n > M_c$, T_{ll} transition of the individual components is observed. This should be expected, since for the component with $M_n < M_c$ the molecules slip one another once there is enough free volume to overcome the secondary cohesive forces, whereas for the component with $M_n > M_c$ a higher temperature is required to break the mechanical entanglement between those molecules. The effect of plasticizers on T_{ll} and T_g are found to be similar[17], which also gives strong support to the free volume basis for the T_{ll} transition.

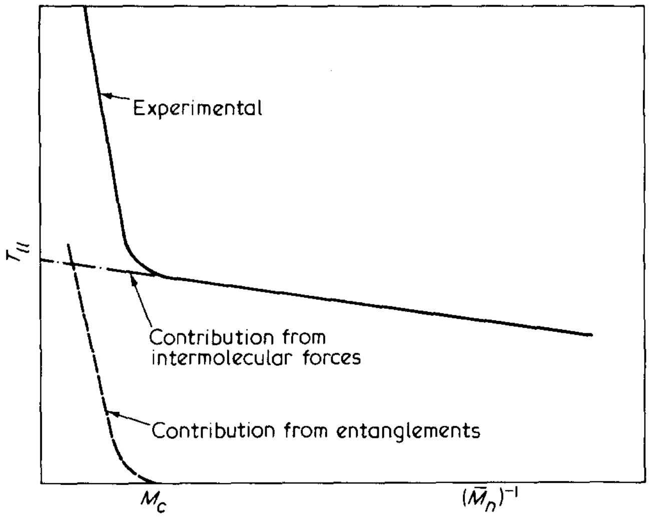

Figure 3 T_{ll} vs. $(\bar{M}_n)^{-1}$. T_{ll} is the temperature at which intermolecular forces and chain entanglement bindings (if $\bar{M}_n > M_c$) are overcome

T_g is usually considered a second-order transition because, for example, the modulus–temperature relationship (shown schematically in *Figure 2*) shows a discontinuity at this temperature. Based on a similar argument, we could consider T_{ll} a third-order transition since the modulus–temperature relationship shows a change in slope instead of a discontinuity at this temperature (as shown shematically in *Figure 2*). This is in agreement with findings of Flory *et al.*[4] and Enns and Boyer[29], who have suggested a third-order transition at T_{ll} due to discontinuities in d^2V/dT^2 and d^2H/dT^2 temperature relationships, respectively.

Tobolsky[30] in his discussion of the five regions of viscoelastic behaviour of linear amorphous polymers has also implicitly referred to the T_{ll} 'transition'. The first three well-known regions are the glassy ($T < T_{g1}$), the leathery ($T_{g1} < T < T_{g2}$), and the rubbery ($T_{g2} < T < T_{r1}$) states. The fourth and fifth regions that we are concerned with here were described as follows: 'In the fourth region the modulus ranges from $10^{6.4}$ to $10^{5.5}$ dynes/cm^2. Here the polymer is elastic and rubbery, but also has a marked component of flow. This may be termed the region of rubbery flow. Finally in the fifth region, with modulus values below $10^{5.5}$ dynes/cm^{-2}, the polymer exhibits very little elastic recovery and manifests a state of liquid flow.' Below T_{r1} the polymer is rubbery with negligible viscous dissipation. At T_{r1} the polymer begins to show flow properties and, hence, the viscous dissipation increases. However, at much higher temperatures the viscous dissipation would decrease again due to lower viscosity values at higher temperatures. Thus, viscous dissipation must go through a maximum at a temperature above T_{r1}. This maximum probably occurs at T_{ll} in the rubbery flow region which separates the rubbery region from the viscous flow region, and is responsible for the peaks observed experimentally in the loss modulus G'' and log (decrement, Δ)[16] and also in loss tangent tan δ[13], since these quantities are related to viscous dissipation. Gillham *et al.*[16], reworking dynamic melt viscosity data of Cox *et al.*[31], have also shown that the dynamic melt viscosity η' ($= G''/\omega$, where ω is angular frequency) of polystyrene goes through a maxiumum above T_g around the expected value for T_{ll}.

The results obtained with the melt elastic tester[5] support the hypothesis that T_{ll} is a rubbery–viscous 'transition'. For example, it is found that the strain recovery curves for polystyrene above its glass transition temperature are of two kinds[5]: 'Type I, below the 'transition' in which the strain recovery is slow, takes a long time and usually reaches a large magnitude, and type II, above the 'transition' in which the recovery is rapid, is completed in a short time and the magnitude of strain recovery is usually small.' Types I and II behaviour of the polymer, as defined above, would be expected if the 'transition' temperatures separating them is considered the rubbery–viscous 'transition' T_{ll}. Below T_{ll}(type I) we would expect high strain recovery since the molecules have high elastic properties, but a slow rate of recovery due to the high viscosity. Above T_{ll} (type II) a small strain recovery is expected since the molecules have lost most of their elasticity, but the rate of recovery should be rapid due to the low viscosity. The processing implications of this 'transition' could be of immense importance. For example, a plastic item moulded below T_{ll} may not be able to relieve most of its internal stresses, whereas processing above T_{ll} could overcome this problem.

CONCLUSIONS

Based on an analysis of the available experimental results and a critical review of the literature, it is suggested that T_{ll} has a molecular origin and can be considered a third-order transition as indicated by the change in slope of the modulus–temperature relationship. It is also argued that the viscous dissipation of an amorphous polymer should go through a maximum in the rubbery-flow region ($T_{r1} < T < T_{r2}$) which separates the rubbery region ($T_{g2} < T < T_{r1}$) from the viscous flow regions ($T > T_{r2}$). The maximim in log (decrement) from t.b.a. results can now be understood as being caused by this maximum in the viscous dissipation rather than being an artifact caused by the braid as suggested by Nielsen[22]. Finally, it is concluded that T_{ll} is the temperature at which the bonds between the molecules break, which causes the major response of the molecules to stress shift from a coiling–uncoiling process (rubbery region) to slippage between the molecules (viscous flow region). For this reason it may be more appropriate to label this transition T_r (the rubbery–viscous transition temperature) rather than T_{ll} (the liquid–liquid transition temperature).

Since this transition occurs both when $M_n > M_c$ and also when $M_n < M_c$, it is hypothesized here that beside the mechanical entanglement between the molecules (which would exist only when $M_n > M_c$) there must exist other cohesive bonds such as hydrogen or van der Waal forces between the molecules, ich are weaker at the T_{ll} temperature.

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