JOURNAL OF MATERIALS SCIENCE 26 (1991) 4281–4284

Characterization of molecular orientation by differential scanning calorimetry

Part 1 T_g–T_{LL} *region for amorphous polymers*

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Differential scanning calorimetry was used to study relaxations occurring above the glass transition, T_g for a number of characterized and fabricated polystyrenes. Part 1 of this study examines the liquid–liquid relaxation temperature, T_{LL}; Part 2 the effects of injection moulding and biaxial orientation of polystyrene; and Part 3 deals with the effects of injection blow moulding.

The rubbery plateau region was found to be bounded by the glass transition, T_g, and a weak transition or relaxation, T_{LL}, found above T_g as an endothermic slope change in the base line. In some cases, this transition could be enhanced as a step change when molten samples were quenched in liquid nitrogen.

The effect of molecular weight on T_g and T_{LL} was similar, and had the relationships $T_{LL}/T_g = 1.07 + 0.03$ for $\bar{M}_w/\bar{M}_n \simeq 1$, and $T_{LL}/T_g = 1.15 \pm 0.01$ for $\bar{M}_w/\bar{M}_n > 1$.

1. Introduction

The existence of a liquid–liquid relaxation above the glass transition (T_g) of amorphous polymers has been well documented. However, because of its elusiveness it is subject to controversy. Evidence for the existence of a transition occurring above the T_g of polystyrene was reported in 1966 [1] and in subsequent publications by Boyer and co-workers using differential scanning calorimetry (DSC) [2–6]. The transition was identified as T_{LL} and occurred at $(1.2 \pm 0.05)\ T_g$ [3, 7]. In later publications Boyer identified a second transition [3] and referred to this transition as T_{LL} [7]. As a result of our own work, we prefer to regard these transitions as relaxations. The origins of these relaxations have not been conclusively determined, but Gillham and Boyer [8] noted that the T_{LL} relaxation was molecularly based. The temperature T_{LL} is determined by the number-average molecular weight for binary blends of polystyrene when both components have molecular weights below the critical molecular weight for chain entanglements (M_c); and homopolymers and diblock and triblock copolymers of styrene have a $T > T_g$ relaxation at approximately the same temperature when the molecular weight of the styrene block is equal to that of the homopolymer [8].

The T_{LL} relaxation has been detected by other techniques including thermomechanical [9] and torsional braid analysis [2, 10–12], but this does not mean that the liquid–liquid relaxations have not had their detractors. It was reported by Nielson [13] that T_{LL} in polymer melts could be an artefact of the torsional braid analysis technique, and Chen *et al.* [14] claimed that the endothermic DSC peaks were a result of volatile components. This was shown to be erroneous by Boyer [15]. Shalaby [16] has presented the pros and cons for the existence of T_{LL}, and Boyer [17] has given an excellent review of the liquid state.

Our interest in the existence of liquid–liquid transitions arose from the observation that on the first heating of polystyrene samples taken from fabricated parts, multiple transitions (relaxations) were present. These appeared to be related to the fabrication conditions and to the molecular weight distribution of the polymer [18].

2. Experimental procedure

All samples were studied by means of a DuPont 910 DSC cell-base with a DuPont 9900 data-control

TABLE I Molecular weight specifications for polystyrene samples produced by Toyo Soda Ltd, Japan

Reference	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A500	5.3×10^2	1.15
A1000	9.5×10^2	1.13
A2500	2.8×10^3	1.05
A5000	6.4×10^3	1.04
F1	1.01×10^4	1.02
F2	1.73×10^4	1.02
F4	4.30×10^4	1.01
F10	9.89×10^4	1.02
F20	1.84×10^5	1.07
F40	4.27×10^5	1.05
F80	7.91×10^5	1.01
F128	1.30×10^6	1.05
685D	3.1×10^5	2.3

station. The temperature and cell-constant calibration was maintained under statistical control using pure indium and mercury standards. The standard deviation in temperature was 0.1 °C and for the cell constant 0.03 J g^{-1}. The sample cell was constantly flushed with nitrogen gas at a flow rate of 50 mL min^{-1}. Samples of 1–2 mg were contained in standard pans with a crimped cover.

The polystyrene was obtained from Toyo Soda Manufacturing, Japan, and was generally used for calibrating gel permeation chromatography columns. The molecular weights and polydispersities are summarized in Table I, together with a commercial polystyrene.

Two methods were used to condition the samples prior to running the DSC scans.

Method 1. The as-received powdered samples were weighed into a DSC pan and placed in the DSC furnace for 1 min at 210 °C. The pan was removed and immediately quenched in liquid nitrogen.

Method 2. The polystyrene samples were flash moulded in a compression mould, weighed into a DSC pan and placed in the furnace for 1 min at 210 °C, followed by a liquid nitrogen quench.

Two consecutive heating scans in the DSC were made on each sample at a scanning rate of 20 °C min^{-1} from − 10 to 210 °C. Free cooling of the sample was undertaken between scans. Some authors have preferred other techniques and scanning rates [19], but the liquid-nitrogen quenching procedure was adopted in order to simulate the rapid cooling experienced in many commercial fabricating processes and our interest in the temperature range between the T_g and normal fabrication temperatures.

Both first and second scans were important, the first being more representative of the structure of the prepared (fabricated) sample, while the second, and sometimes the third scan, was necessary to reveal structural effects in an annealed sample. Each sample was tested a number of times. Boyer [7] has adopted a technique for measuring the intensity of liquid–liquid transitions by the angle of the endothermic slope change at the transition, expressed in radians per 100 mg of sample. The literature attests to the elusiveness of the liquid–liquid transition and so, for the present purposes, we decided to record only those data that were not open to subjective interpretation.

3. Results

The glass temperature, T_g, does not occur at a single temperature but is in fact a temperature range of 15–20 degrees in which the onset of motion on the scale of molecular displacements can be detected in a polymer sample. The fact that one temperature is reported as T_g is a matter of convenience. In the present case, we have selected a midpoint temperature between two inflections, T_a and T_c, of the base line recorded during the transition (Fig. 1). Other authors have chosen point T_b. Fig. 1 also shows T_{LL} as a slope change.

Whereas powdered samples showed T_g as a step change and T_{LL} as a slope change, both relaxations were seen as step changes for compression-moulded samples. On second heating scans, the T_{LL} step change disappeared and was observed as a slope change.

The intensity of the slope, θ rad mg^{-1}, was of the same order as observed by Boyer [7] and actually corresponded to a 3-5-degree slope change in the base line. The data are presented in Table II. T_g and T_{LL} are plotted as a function of molecular weight in Fig. 2 and have the empirical relationship

$$T_{LL}/T_g = 1.07 \pm 0.03 \qquad (1)$$

A number of DSC scans were carried out on different samples of a commercially available, broad-molecular-weight distribution polystyrene. The results are presented in Table III. The intensities of T_{LL} were of the same order as the narrow molecular weight distribution samples, and T_g was as expected. In all cases T_{LL} was observed as an endothermic slope change in the scan. The relationship between T_g and T_{LL} was calculated as

$$T_{LL}/T_g = 1.15 \pm 0.01 \qquad (2)$$

which is in agreement with Boyer [17] if one takes $T_g \equiv T_b \equiv 374$ K (Fig. 1)

$$T_{LL}/T_g = 1.16 \qquad (3)$$

Two samples, A2500 and F128, which had previously shown a step change at T_{LL} when cooled in liquid nitrogen, were dry blended to give an average molecular weight similar to the commercial sample, 685D. The dry blend was scanned four times, with air cooling between each cycle. T_{LL} was not observed, but the T_g of the individual functions was detectable even after the fourth heating cycle. The same mixture was dissolved in tetrahydrofuran and a film prepared by drying under vacuum. The T_g of the blend followed the Fox equation for mixtures [18], while an enhanced T_{LL} was visible as a strong change in slope after the second heating cycle. Recently, a similar observation was reported by Chang [20], who assumed the mul-

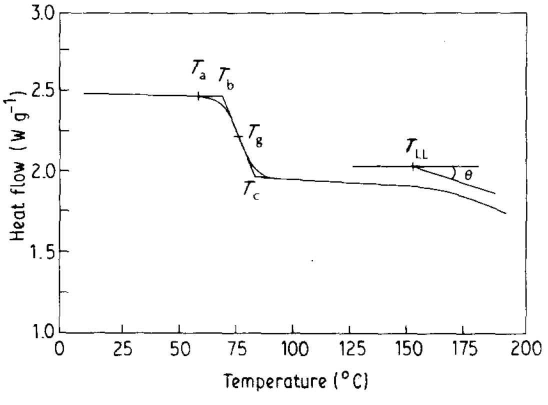

Figure 1 Example DSC scan for T_g and T_{LL} determination.

TABLE II DSC data for $\bar{M}_w/\bar{M}_n \simeq 1$

		Method 1			Method 2			
Reference No.	T_g(K)[a]	T_{LL} (K)[b]	θ[c]	T_{LL}/T_g	T_{LL} (K)[d]	T_{LL} (K)[e]	θ[c]	T_{LL}/T_g[f]
A500	241	278	–	1.15	–	–	–	–
A2500	344	376	6.6	1.10	357	358	3.8	1.05
A5000	362	373	1.5	1.03	379	380	3.9	1.05
F1	369	378	6.5	1.03	383	383	4.4	1.04
F2	374	405	1.6	1.08	–	–	–	–
F4	377	413	5.7	1.10	395	398	4.8	1.06
F10	378	410	7.1	1.09	–	400	3.0	1.06
F20	379	418	6.5	1.10	–	395	5.6	1.04
F40	379	409	2.8	1.08	–	401	2.0	1.06
F60	378	397	4.2	1.05	–	395	5.7	1.05
F128	379	416	4.7	1.10	399	400	3.9	1.06

[a] T_g, second heat of powder.

[b] Measured as slope change on first scan of powders; no slope change on second heat.

[c] θ, intensity of slope change, radians/100 mg.

[d] T_{LL} appeared as step change in base line, after nitrogen quench.

[e] Slope change on second heat of moulded samples.

[f] T_{LL}/T_g = column 5/column 1.

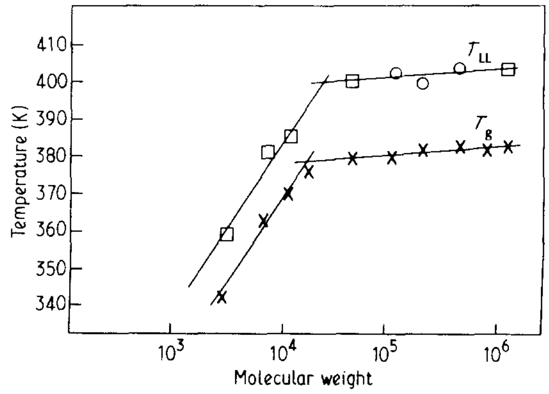

Figure 2 T_g against molecular weight and T_{LL} against molecular weight for $\bar{M}_w/\bar{M}_n \simeq 1$. □, Step change for T_{LL}; ○, slope change for T_{LL}; x, T_g.

TABLE III DSC data for $\bar{M}_w/\bar{M}_n > 1$: sample 685D

Sample	T_g(K)[a]	T_{LL}(K)[a]	T_{LL}/T_g
Powder	378	435	1.15
	379	433	1.14
Powder/N_2 cooled	378	436	1.15
Film/N_2 cooled	379	438	1.16
	380	435	1.14
	379	435	1.15
	378	431	1.14
Film annealed	375	431	1.15
Film	375	431	1.15
Averages	378 ± 1.15	434 ± 2.5	1.15 ± 0.01

[a] Determined from first scan.

TABLE IV DSC data for binary blend 1, $\bar{M}_w/\bar{M}_n > 1$

Scan	T_{g_1} (K)	T_{g_2} (K)	T_{LL} (K)
Powder no. 1	344	377	–
2	344	377	–
3	345	378	–
4	344	377	–
THF dissolved	357	–	428

tiple transitions were due to non-uniform distribution or relaxation times. T_{LL} and T_g followed Equation 3, Table IV.

4. Discussion

Studies of the increase in T_g with increasing molecular weight date back to the work of Ueberreiter [21] and the theoretical analysis of Fox and Flory [18, 22]. It has been established by dilatometric techniques with polystyrene fractions of low volatile content, that T_g is given by Equation 5, where K_g is a polymer-specific constant and $T_g(\infty)$ is the asymptotic limiting value of T_g at high $\bar{M}$.

$$T_g = T_g(\infty) - K_g\bar{M}_n^{-1} \qquad (5)$$

The T_g–$\bar{M}_n$ relationship (Fig. 2) could equally be represented by a polynomial, but as pointed out by Boyer [17] information may be lost.

Cowie [23] studied the variation of T_g with molecular weight from oligomers up and noted that the data could be represented by three straight intersecting lines. We have chosen two because of the lack of data at low molecular weight, but it is noted that the two lines intersect at a point corresponding to a characteristic entanglement molecular weight.

The corresponding T_{LL}–$\bar{M}_n$ relationship can also be represented by two intersecting straight lines. There is still some reluctance to accept T_{LL} as real, but there is overwhelming evidence in the literature for the existence of a super-glass transition or relaxation occurring above the T_g. Boyer has given a comprehensive review [17] and the pros and cons need not be pursued here, except to comment that they are indeed difficult to detect. Both our work and that of Kokta *et al.* [24] has shown that rapid cooling enhances the relaxation in some cases, but the very nature of the elusiveness of T_{LL} casts doubt on the 'purity' of the narrow-molecular-weight distribution samples so often used. The fact that T_{LL} may be detected as an endothermic slope change rather than a step change for broad molecular weight samples (685D and blend 1) may offer a clue.

The present work does not attempt to elucidate the mechanism or nature of the structural changes occurring between T_g and T_{LL} but our studies [25, 26] do indicate the importance of this temperature region to enhance the orientational properties of polystyrene.

5. Conclusion

Differential scanning calorimetry may be used to detect the liquid–liquid transition, T_{LL}, in amorphous polymers. Rapid quenching and annealing experiments indicated that the origin of the transition was one of molecular orientation.

Acknowledgement

I would like to thank Mr C. Shaw for generating the DSC data and the Dow Chemical Company for permission to report the work.

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Received 10 October 1989
and accepted 26 October 1990