# Thermal properties and physical ageing of poly(L-lactic acid)

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Poly(L-lactic acid) (PLLA) was investigated by differential scanning calorimetry and dynamic mechanical and dielectric spectroscopies. In the dynamic mechanical and dielectric spectra no secondary relaxations were observed below the glass-to-rubber transition (70°C at 3 Hz). The thermal history strongly affects the physical properties of PLLA, inducing changes of crystalline:amorphous ratio as well as large physical ageing effects on the glassy amorphous phase. This latter phenomenon is clearly observed as a consequence of room-temperature storage and develops at a faster rate as the ageing temperature $T_a$ approaches $T_g$. Ageing experiments carried out at the same undercooling ($\Delta T = T_g - T_a$) on PLLA samples of different molecular weight ($\bar{M}_v = 5300$, 20 000, 691 000) show that a decrease in molecular weight increases the magnitude of the enthalpy relaxation at the glass transition.

**(Keywords: poly(L-lactic acid); physical ageing; thermal properties)**

## INTRODUCTION

Interest in polylactide materials has rapidly grown in recent years and a number of papers have highlighted the remarkable properties of these polymers for applications in the medical field: compatibility with biological tissues[1,2], degradability *in vivo* and *in vitro*[3–6], and good mechanical characteristics[7–9].

Some physical properties of polylactides have been extensively investigated: crystalline structure[10–12], molecular conformation[11,12] and morphology and crystallization kinetics[13–16]. However, little attention has been paid to their thermal properties. In fact the thermal data available are confined to calorimetric characterization of glycolic–lactic acid copolymers[17] as well as of poly(DL-lactic acid) (PDLLA) and poly(L-lactic acid) (PLLA)[18].

As far as PLLA is concerned, no viscoelastic data have been reported so far, although knowledge of the relaxation processes that make up the viscoelastic spectrum and of their dependence on thermal history is undoubtedly relevant to the practical applications of polylactides.

Among the aims of this paper are to provide dynamic mechanical and dielectric characterization of the optically active poly(L-lactic acid), and to investigate the effect of 'physical ageing' on the properties of the polymer, considering ageing time, temperature, and polymer molecular weight as variable parameters.

## EXPERIMENTAL

Three samples of poly(L-lactic acid) (PLLA) of different molecular weights were used in this work. One sample ($\bar{M}_v = 5300$), synthesized by direct polycondensation of lactic acid in xylene, was kindly supplied by Dr G. Perego of Himont Italia (Centro Ricerche Novara). The remaining samples ($\bar{M}_v = 20\,000$, trade name Resomer L206, and $\bar{M}_v = 691\,000$, Resomer L214) were purchased from Boehringer. The samples are referred to as A, B and C in order of increasing molecular weight, as indicated in *Table 1*.

Dynamic mechanical measurements were performed with a DMTA (Polymer Laboratories Ltd) operated in the dual cantilever bending mode, at a frequency of 3 Hz and a heating rate of 3 K min$^{-1}$. PLLA samples in the form of small bars, injection-moulded at 250°C, were investigated in the temperature range from −150 to 160°C.

Dielectric measurements were carried out with a DETA instrument (Polymer Laboratories Ltd), at a heating rate of 1 K min$^{-1}$ at five selected frequencies (0.3, 1, 3, 10, 50 kHz), on films (40 μm thick) of sample C prepared by casting 1 wt% chloroform solutions on to glass plates. Before measurement, the sample was heated under vacuum to 120°C in the DETA to eliminate absorbed water.

Calorimetric (d.s.c.) measurements were performed on as-received powder samples by means of a DuPont 9900 Thermal Analysis System (heating rate 10 and 20 K min$^{-1}$) in the temperature range from −80 to 200°C. The temperature scale was calibrated with high-purity standards. The glass transition temperature ($T_g$) was taken as the inflection point of the specific heat increment.

Ageing experiments at selected temperatures ($T_a$) were performed as follows: each sample was heated to 200°C at 20 K min$^{-1}$ in order to erase the previous thermal history, then rapidly cooled to $T_a$. After ageing at $T_a$ for a chosen time ($t_a$), the sample was rapidly quenched to −80°C and subsequently heated at 20 K min$^{-1}$ to above

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**Table 1** Physical properties of poly(L-lactic acid)

| Sample | $\bar{M}_v$ | $T_m$[a] (°C) | $\Delta H_m$[a] ($J g^{-1}$) | $T_g$[b] (°C) | $\Delta C_p$[b] ($J g^{-1} K^{-1}$) |
|---|---|---|---|---|---|
| A | 5300 | 156 | 61 | 55 | 0.60 |
| B | 20000 | 174 | 68 | 59 | 0.54 |
| C | 691000 | 186 | 59 | 64 | 0.54 |

[a] By d.s.c., 10 K $min^{-1}$
[b] By d.s.c., 20 K $min^{-1}$

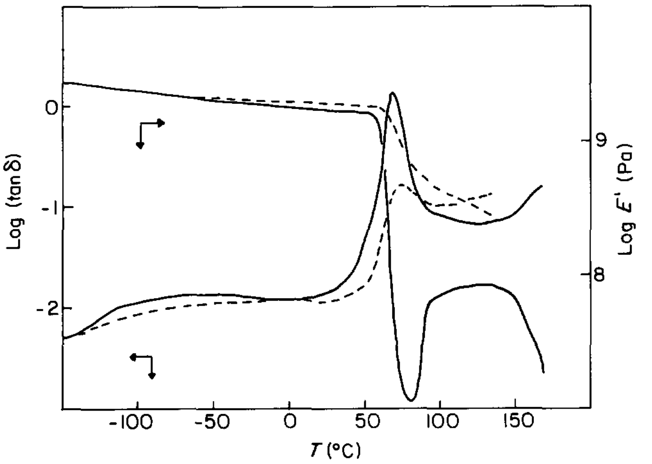

**Figure 1** Dynamic mechanical spectrum of poly(L-lactic acid) (sample C): (——), first run; (- - -) second run

the glass transition. Because unexpectedly low $T_g$ values were occasionally observed after several high-temperature heating cycles, fresh polymer sample was used for each ageing experiment.

## RESULTS AND DISCUSSION

The dynamic mechanical spectrum of PLLA is shown in *Figure 1*: the temperature-dependences of the loss tangent (tan $\delta$) and of the storage modulus ($E'$) are shown for the high-molecular-weight polymer (sample C); the lower-molecular-weight PLLA samples (A and B) were very fragile and underwent brittle fracture during measurement below room temperature, so no reliable viscoelastic results could be obtained over the whole temperature range.

In *Figure 1* two different curves are shown: the solid line refers to a sample quenched from the melt in a water–ice mixture after extrusion, whereas the broken line relates to an immediate rerun on the same sample, after cooling from 160°C. Below room temperature no relaxation process is apparent in either curve: the dynamic mechanical loss tangent is as low as $10^{-2}$ over the range −150 to 20°C. The absence of any loss phenomena below $T_g$ capable of mechanical energy dissipation is likely to explain the observed brittleness of glassy PLLA and induce catastrophic failure of the low-molecular-weight samples.

In the first run on quenched PLLA, the loss tangent curve shows a very intense relaxation peak in the range 50–80°C (peak value 70°C), associated with a very steep drop in modulus; this relaxation phenomenon corresponds to the glass-to-rubber transition of PLLA, and its intensity indicates that a very large fraction of the sample has been frozen in the glassy amorphous state after extrusion. The location of the glass transition agrees with published values[18]. The abrupt increase in $E'$ above 80°C reflects a sudden increase in rigidity of the material and indicates that, above $T_g$, the polymer chains have acquired enough mobility to crystallize during the dynamic mechanical run.

The occurrence of crystallization is clearly demonstrated by the spectrum obtained in an immediate rerun (broken line in *Figure 1*), where the glass transition of PLLA appears as a tan $\delta$ peak of moderate intensity associated with a fairly small decrease in the storage modulus. In this instance only a small fraction of the sample undergoes the glass transition, owing to the presence of a significant crystalline phase. The crystallites, acting as 'physical crosslinks', cause the observed broadening of the tan $\delta$ peak. *Figure 2* shows the multifrequency dielectric spectrum of PLLA (sample C); as already noted in the dynamic mechanical spectrum of *Figure 1*, no relaxation phenomena are observed below the glass transition, which appears in *Figure 2* as a dielectric peak whose temperature increases with increasing frequency.

Although the Arrhenius equation

$$\ln \nu = \ln \nu_0 - E_a/RT \qquad (1)$$

correctly describes only the frequency-dependence of the peak temperature of *secondary* relaxations, the insert in *Figure 2* shows that in the case of the glass transition of PLLA the ln $\nu$ *versus* $1/T$ plot is satisfactorily linear. The value of the apparent activation energy $E_a$ calculated from the slope of the line is ≈420 kJ $mol^{-1}$, a reasonable value for a glass transition phenomenon. The insert in *Figure 2* also contains the peak value of the dynamic mechanical glass transition. It can be seen to lie on the line drawn through the dielectric results, confirming that the linear behaviour extends over a wide frequency range.

Differential scanning calorimetry was used to investigate both the glass transition and the melting of PLLA. As an example, *Figure 3* shows two d.s.c. curves of sample B: the first run (curve A) and an immediate rerun (curve B) after quenching from 200°C to −80°C. The as-received PLLA powder is partly crystalline, and the glass transition cannot be clearly revealed by d.s.c. The

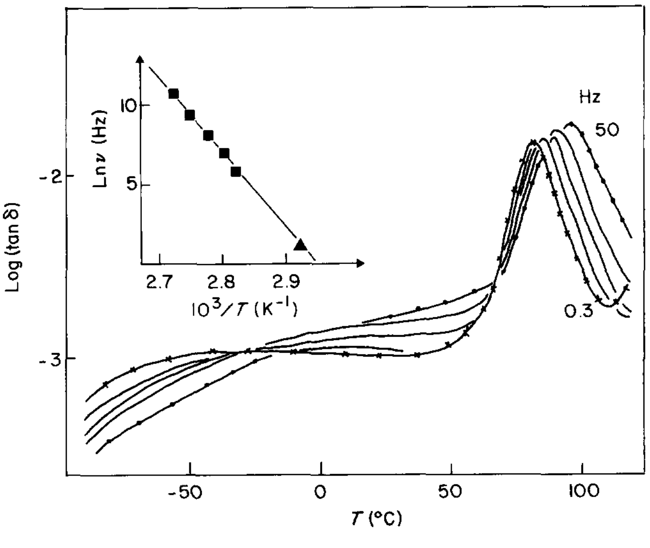

**Figure 2** Multifrequency dielectric spectrum of poly(L-lactic acid) (sample C) at frequencies of 0.3, 1, 3, 10 and 50 kHz. Insert: Arrhenius plot: (■), dielectric; (▲) dynamic mechanical

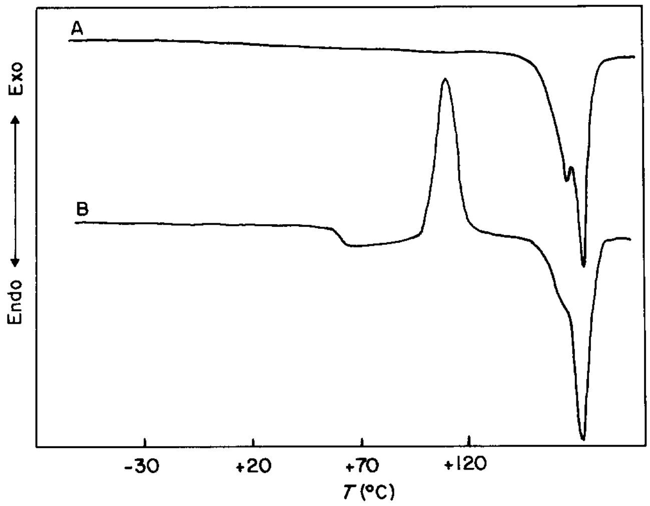

**Figure 3** D.s.c. curves of poly(L-lactic acid) (sample B): (A) first scan; (B) second scan, after quenching from the melt. Heating rate 20 K min$^{-1}$

only significant feature in curve A is in fact the complex melting endotherm showing two peaks at 165 and 172°C.

As already mentioned in connection with the dynamic mechanical results of *Figure 1*, quenching from the melt inhibits PLLA crystallization and 'freezes' samples in the glassy amorphous state; in curve B of *Figure 3*, a large endothermal baseline shift clearly indicates the glass transition of amorphous PLLA in the vicinity of 60°C. Comparison of the experimental value of the specific heat increment at $T_g$ (see *Table 1*) with that predicted by Wunderlich's rule[19] confirms that after quenching, practically all the PLLA sample is in the amorphous state and undergoes a glass transition.

Above the transition, in curve B an exothermic peak associated with a 'cold crystallization' process appears. It is the crystalline phase formed during this process that melts at higher temperature, showing an endotherm with a main peak at 173°C preceded by a shoulder. The heat of fusion, $\Delta H$, associated with this melting endotherm is lower than that obtained in the first scan (55 *versus* 71 J g$^{-1}$): this result indicates that, at the heating rate employed (20 K min$^{-1}$), during cold crystallization the sample cannot crystallize to the same extent as does the original PLLA powder.

The calorimetric behaviour of sample A is very similar to that shown by sample B in *Figure 3*. Sample C, on the other hand, displays a much reduced ability to crystallize above $T_g$ during the second scan, owing to its high molecular weight, which decreases chain mobility at $T > T_g$. As for the temperature of the glass transition, the calorimetric $T_g$ values reported in *Table 1* decrease with decreasing molecular weight, as expected.

It was interesting to observe in the present work that, if amorphous PLLA samples are left at room temperature after quenching from the melt, an endothermic peak develops near the glass transition for all molecular weights examined. This is illustrated in *Figure 4* for sample B, tested after 6 days of storage at room temperature. As already shown in *Figure 3* (curve B), the peak is absent in immediate reruns and can be attributed to enthalpy relaxation effects related to the thermal history of the sample.

When a polymer is quenched from the melt and vitrifies, a non-equilibrium glassy state is reached[20]. Even in the glass, short-range mobility produces molecular rearrangements that drive the thermodynamic variables closer to their equilibrium values. Thus if a polymer is annealed below $T_g$, it evolves towards the equilibrium state, a hypothetical condition attained only after an infinitely long time[21,22].

Since the enthalpy of the polymeric glass decreases with time, the thermal properties reflect the occurrence of ageing, as already shown in *Figure 4* and further illustrated in *Figure 5*, where the calorimetric curves of sample B after annealing at $T_a = 30$°C for times ($t_a$) varying from 0 to 22 h are shown. A method of quantifying the consequences of ageing for the glass transition is to evaluate the 'excess enthalpy relaxation' $\Delta H$. This can be done[23,24] by integrating between two temperatures well below and well above the transition (in the 'glass' and 'liquid' regions respectively) the experimental $\Delta C_p$ 'difference curve', obtained by subtracting from the heat capacity curve of each 'aged' sample, that of the 'unaged' polymer ($t_a = 0$). $\Delta H$ is plotted in the insert of *Figure 5* and – to a first approximation – seems to display a linear dependence on log $t_a$. The experimental data available are insufficient to attempt a more complete analysis of the phenomenon on the basis of the available phenomenological models[24–26].

Besides ageing time, the temperature at which the ageing experiment is performed is also a very important parameter in determining the extent of the ageing effect. The mobility of the polymer chains, i.e. the ability to eliminate excess free volume, is directly related to temperature. The effect of the ageing temperature on enthalpy relaxation is shown in *Figure 6* for sample C. Curves for PLLA annealed for 22 h at $T_a$ = 30, 40 and 48°C are shown together with that of the 'reference' unannealed sample. In the temperature range explored, after the same ageing time the relaxation effect on the glass transition increases with increasing temperature, $\Delta H$ being equal to 2.0, 2.9 and 3.8 J g$^{-1}$ at 30, 40 and 48°C respectively. This result is a consequence of the rate-controlling effect of temperature on the ageing process. Although the extent of the enthalpy change on annealing is predicted to increase with decreasing temperature, exceedingly long times are required to

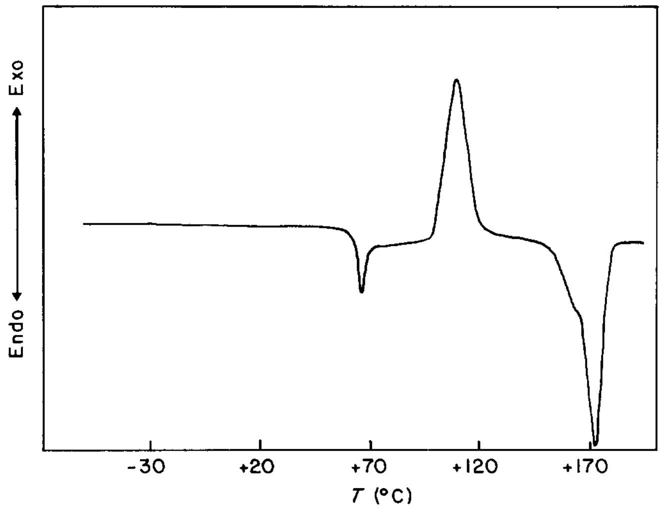

**Figure 4** D.s.c. curve of poly(L-lactic acid) (sample B) after 6 days at room temperature after quenching. Heating rate 20 K min$^{-1}$

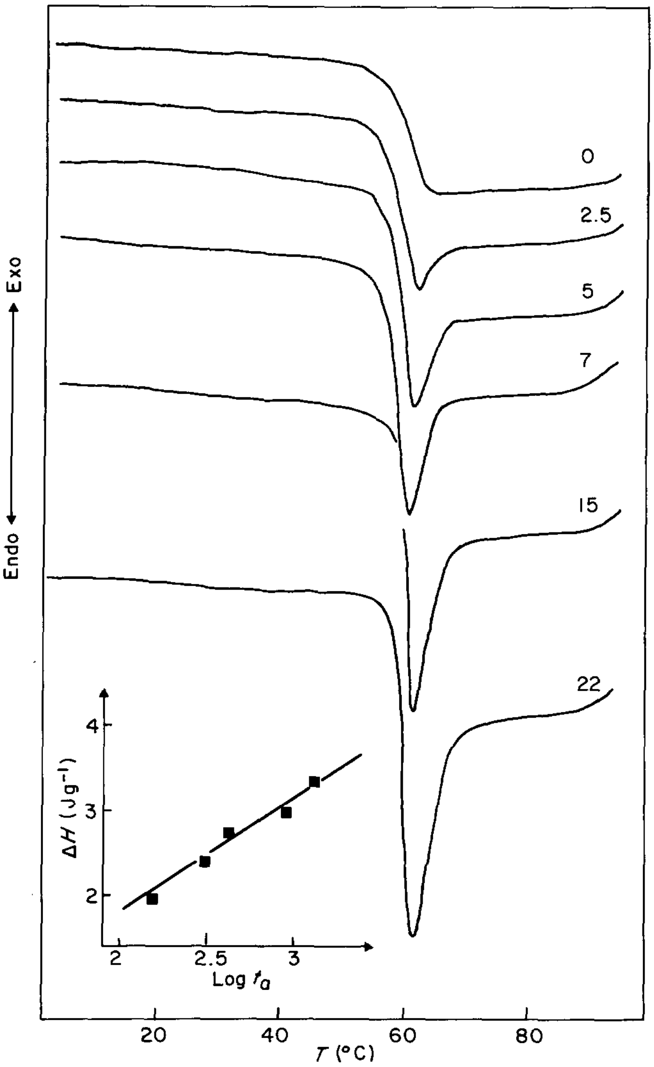

**Figure 5** D.s.c. curves in the glass-transition region of poly(L-lactic acid) (sample B) annealed for different times $t_a$ at $T_a = 30°C$, heating rate 20 K min$^{-1}$. Insert: excess enthalpy relaxation $\Delta H$ as a function of ageing time

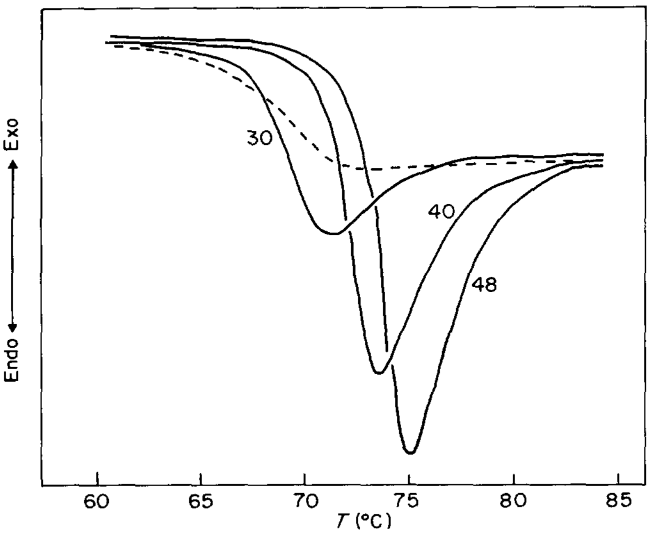

**Figure 6** D.s.c. curves in the glass transition region of poly(L-lactic acid) (sample C) annealed for 22 h at different temperatures $T_a$; (– – –) 'reference' unannealed sample. Heating rate 20 K min$^{-1}$

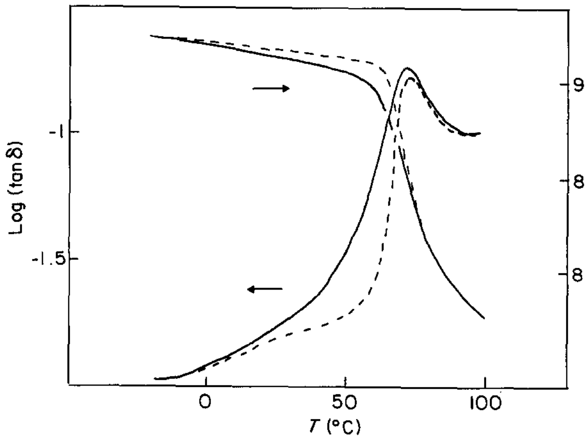

**Figure 7** Influence of ageing on the dynamic mechanical spectrum of PLLA. Ageing time: (——), zero; (– – –) 9 days at 48°C

reduce the enthalpy by a given amount as the subcooling ($\Delta T = T_g - T_a$) increases. For this reason, in the experimentally accessible time-scale the effect of physical ageing is seen to vanish at temperatures well below $T_g$.

The effect of ageing on the dynamic mechanical properties of PLLA was investigated for sample C, the ageing temperature being selected on the basis of the indications obtained from the d.s.c. experiments. *Figure 7* shows how the glass transition region of the viscoelastic spectrum of PLLA is modified by ageing: the broken curves refer to a sample aged 9 days at 48°C, while the solid lines are the reference curves (ageing time $t_a = 0$) obtained in an immediate rerun of the same sample, after cooling from 100°C.

The PLLA sample used for the ageing experiment was partly crystalline, and the heat treatment up to 100°C was intended to erase the previous thermal history without changing the amorphous:crystalline ratio. The differences observed in *Figure 7* are therefore entirely due to ageing, the net effect of which is to decrease the loss factor and to increase the storage modulus over the whole low-temperature branch of the transition. As a result of ageing, the mechanical characteristics of PLLA change: the ability to dissipate energy through molecular motion decreases and the rigidity increases, resulting in a more brittle material.

As already pointed out in connection with *Figure 6*, as the subcooling with respect to $T_g$ increases, the effect brought about by ageing for a given time decreases. It can be easily predicted therefore that storage of PLLA for a comparable time at room temperature will produce less dramatic changes than those shown in *Figure 7*, though significant effects must be expected if the storage time becomes long enough.

Finally, the effect of molecular weight on the ageing process of PLLA was investigated. The above discussion on the dependence of ageing on the value of $T_a$ implies that, in order to obtain comparable results on PLLA samples with different $T_g$ values (see *Table 1*), experiments have to be performed at the same degree of subcooling.

Marshall and Petrie[25] have shown that, at corresponding temperature intervals below $T_g$, the enthalpy relaxation of glassy atactic polystyrene is a function of molecular weight ($\bar{M}$) and that the rate of enthalpy relaxation becomes independent of $\bar{M}$ in the same range of $\bar{M}$ values as that in which the $T_g$–$\bar{M}$ dependence levels

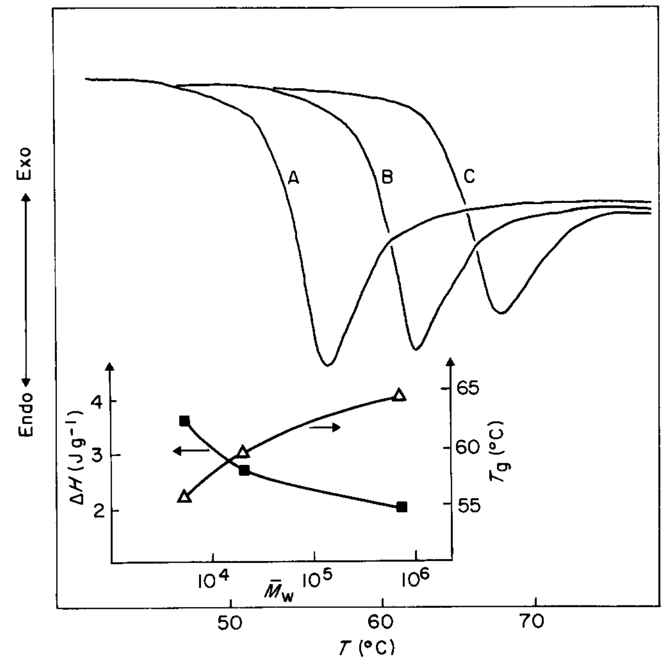

**Figure 8** D.s.c. curves in the glass transition region of poly(L-lactic acid) (samples A, B and C) annealed for 1 h at the same degree of subcooling. Ageing temperature: (A) 40°C; (B) 44°C; (C) 49°C. Heating rate of 20 K $\mathrm{min}^{-1}$. Insert: excess enthalpy relaxation $\Delta H$ and $T_g$ as a function of molecular weight

off. *Figure 8* shows the d.s.c. curves in the glass transition region of samples A, B and C after annealing for 1 h at 40, 44 and 49°C respectively, i.e. at the same degree of subcooling $\Delta T = -15$°C. The relaxation enthalpy $\Delta H$ is found to increase with decreasing molecular weight, as illustrated in the insert, where also $T_g$ (from *Table 1*) is plotted as a function of $\bar{M}_v$. The observed increase of $\Delta H$ with decreasing $\bar{M}_v$ can be attributed to the greater ability of short polymer chains to relax free volume. This is due to the larger proportion of chain terminals that possess higher motional freedom than internal chain segments. The additional free volume associated with the chain ends also causes the observed $T_g$–$\bar{M}_v$ dependence. The present interpretation is in line with that previously proposed[25] to explain the molecular weight dependence of the enthalpy relaxation process in polystyrene.

## CONCLUSIONS

It has been shown how thermal history affects the viscoelastic spectrum and thermal properties of PLLA. In particular, the phenomenon of 'physical ageing' below $T_g$ has been investigated in detail.

For PLLA samples of different molecular weight, the effect of ageing has been found to depend not only on ageing temperature but also – at comparable subcooling – on molecular weight. As a result of ageing, below the glass transition the rigidity of PLLA increases and its damping capacity decreases, causing embrittlement of the polymer. Since significant ageing effects are produced over the whole range from room temperature up to near $T_g$, whenever PLLA is stored at any temperature in this range, a change of properties with time has to be expected.

It is widely recognized that poly(L-lactic acid) is a potential candidate for a number of practical applications as a biodegradable and biocompatible thermoplastic. The present results have important implications for the use of PLLA in the medical field, highlighting the fact that at physiological temperatures, ageing can produce conspicuous effects on the polymer properties.

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## REFERENCES

1 Lipinsky, E. S. and Sinclair, R. G. *Chem. Eng. Progr.* 1986, **82**, 26
2 Vert, M. *Angew. Makromol. Chem.* 1989, **166–167**, 155
3 Reed, A. M. and Gilding, D. K. *Polymer* 1981, **22**, 494
4 Chawla, A. S. and Chang, T. M. S. *Biomater., Med. Dev., Art. Org.* 1985–86, **13**, 153
5 Leenslag, J. W., Pennings, A. J., Bos, R. R. M., Rozema, F. R. and Boering, G. *Biomaterials* 1987, **8**, 311
6 Nakamura, T., Hitomi, S., Watanabe, S., Shimizu, Y., Jamshidi, K., Hyon, S.-H. and Ikada, Y. *J. Biomed. Mater. Res.* 1989, **23**, 1115
7 Eling, B., Gogolewski, S. and Pennings, A. J. *Polymer* 1982, **23**, 1587
8 Gogolewski, S. and Pennings, A. J. *J. Appl. Polym. Sci.* 1983, **28**, 1045
9 Leenslag, J. W., Pennings, A. J., Bos, R. R. M., Rozema, F. R. and Boering, G. *Biomaterials* 1987, **8**, 70
10 Liquori, A. M., de Santis, P., Kovacs, A. J. and Mazzarella, L. *Nature* 1966, **211**, 1039
11 De Santis, P. and Kovacs, A. J. *Biopolymers* 1968, **6**, 299
12 Hoogsteen, W., Postema, A. R., Pennings, A. J., ten Brinke, G. and Zugenmaier, P. *Macromolecules* 1990, **23**, 634
13 Kalb, B. and Pennings, A. J. *Polymer* 1980, **21**, 607
14 Vasanthakumari, R. and Pennings, A. J. *Polymer* 1983, **24**, 175
15 Kishore, K. and Vasanthakumari, R. *Colloid Polym. Sci.* 1988, **266**, 999
16 Jorda, R. and Wilkes, G. L. *Polym. Bull.* 1968, **19**, 409
17 Gilding, D. K. and Reed, A. M. *Polymer* 1979, **20**, 1459
18 Jamshidi, K., Hyon, S.-H. and Ikada, Y. *Polymer* 1988, **29**, 2229
19 Wunderlich, B. *J. Phys. Chem.* 1960, **64**, 1052
20 Haward, R. N. (ed.). 'The Physics of Glassy Polymers', Applied Science, London, 1973
21 Petrie, S. E. B. *J. Polym. Sci. A-2* 1972, **10**, 1255
22 Struik, L. C. E. In 'Physical Aging of Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
23 Richardson, M. J. and Savill, N. G. *Polymer* 1975, **16**, 753
24 Cowie, J. M. G. and Ferguson, R. *Macromolecules* 1989, **22**, 2307
25 Marshall, A. S. and Petrie, S. E. B. *J. Appl. Polym. Sci.* 1975, **46**, 4223
26 Hodge, I. M. and Berens, A. R. *Macromolecules* 1982, **15**, 762