

Dynamic Mechanical and Calorimetric Analysis of Compression-Molded PLLA of Different Molecular Weights: Effect of Thermal Treatments

C. MIGLIARESI,^{1,*} D. COHN,² A. DE LOLLIS,³ and L. FAMBRI¹

¹Dipartimento di Ingegneria dei Materiali, Università di Trento, Italy, ²Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Israel, and ³Officine Ortopediche Rizzoli Bologna, Italy

SYNOPSIS

The effect of thermal treatment on compression-molded poly(L-lactic acid) (PLLA) has been investigated by means of viscosimetric molecular weight (M_w) determination, differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA). Starting from two initial molecular weight PLLAs, amorphous samples with different M_w have been obtained due to degradation occurring during the molding. The crystallization capability of the materials after different thermal treatments has been determined as a function of the molecular weight, and their dynamic mechanical properties have been measured. Initially fully amorphous PLLA matrices attained very high degrees of crystallinity (up to 90%) following different annealing processes. Concomitantly, PLLA degrades due to thermal cleavage of the chains. This is an unavoidable effect that must be taken into consideration when defining the material processing and annealing conditions. Crystallization phenomena occurring in the material during the treatment are clearly documented by DMTA.

INTRODUCTION

Development of new biodegradable polymers has attracted much attention in recent years, mainly due to their increasing clinical demand.^{1,2} The advantages of biodegradable implants pertain to both the quality of the healing process at the implantation site and to the fact that there is no need for a second operation to remove the device.

Poly(lactic acid) (PLA) has been, since it was synthesized, one of the most important biodegradable polymers.³⁻⁵ It represents the preferred alternative to polyglycolic acid⁶⁻⁸ whenever slower degradation kinetics are required. Numerous researchers have investigated different aspects of this polymer, including its synthesis, morphology, and

mechanical properties, as well as its degradation kinetics under both *in vitro* and *in vivo* conditions.⁹⁻¹⁴ Efforts have also been invested in developing biomedical systems based on PLA, especially for orthopedic applications¹⁵⁻¹⁷ and controlled drug delivery systems.^{18,19}

Notwithstanding the fact that PLA is very successful in various uses, there are still numerous clinical areas in which PLA cannot perform, mainly due to mechanical limitations. The often excessively fast degradation kinetics of PLA was overcome, to a given extent, by using the L-enantiomeric form^{16,20} and high molecular weight poly(L-lactic acid) (PLLA) chains.^{17,21,22}

This introductory work is part of a broader research program aiming at investigating the relationship between the mechanical properties and morphological characteristics of PLA and its biodegradation kinetics. It is part of a more comprehensive research conducted by several laboratories, focused on both the improvement of PLA mechanical properties, as well as the control of its degree

* To whom correspondence should be addressed at Dipartimento di Ingegneria dei Materiali, Università di Trento, 38050 Mesiano di Povo, Trento, Italy.

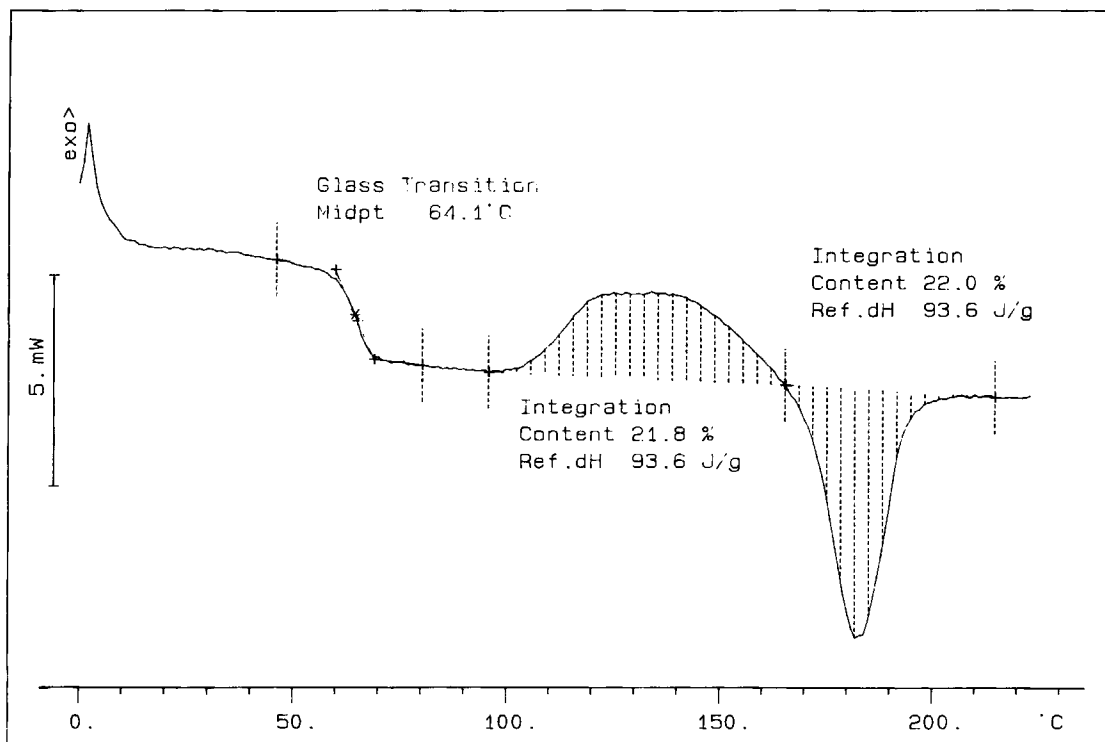


Figure 1 DSC thermogram of an amorphous PLLA with molecular weight of 85,000.

of crystallinity, so different degradation kinetics could be obtained. The present article deals with the effect of thermal treatments and processing conditions on the degree of crystallinity of PLLA and their molecular weight. Light will be shed on the difficulties inherent to thermal instability of PLLA, which seriously limits the merits of thermal treatments as a way to engineer improved PLA biodegradable devices.

EXPERIMENTAL

Materials

Samples have been prepared by compression molding of poly-L-lactic acid obtained from Boehringer,

Table I Molecular Weight Before (Initial) and After Molding of Investigated PLLA Samples

Sample	M_{w_0} Initial	M_{w_0} After Molding
PLA230	440,000	230,000
PLA200		200,000
PLA68		68,000
PLA85	300,000	85,000
PLA40		37,000–41,000

Ingelheim, or synthesized from L-lactide in our laboratory following the procedure described in ref. 23. PLLA with initial molecular weights of 440,000 and 300,000 were used.

PLLA sheets ($10.0 \times 5.0 \times 0.15 \text{ cm}^3$) were compression molded at a temperature of 210°C . After molding, samples were quenched by circulating cold water in the mold plates and over the polymer dye. Care was taken to avoid any contact between the polymer and water.

Specimens with dimensions of $5.0 \times 1.0 \text{ cm}^2$ were cut from the different sheets and stored under vacuum in a desiccator until use.

Methods

Differential scanning calorimetry was performed by using a Mettler DSC 30 calorimeter, at a heating

Table II Molecular Weights, M_{w_0} , of PLA230 (I) and PLA40 (II) Treated at 160°C for Different Times

Sample	Time (h)				
	0	1/4	1	20	90
I	230,000	185,000	180,000	110,000	64,000
II	41,000	34,000	25,500	24,000	17,000

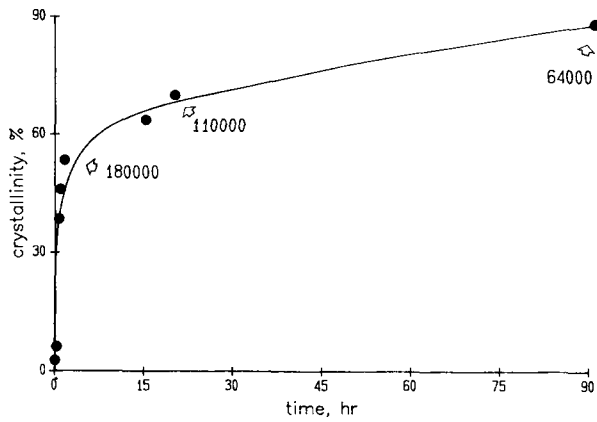


Figure 2 Crystallinity degree and molecular weight of PLA230 as a function of the duration of the thermal treatment at $T = 160^{\circ}\text{C}$.

rate of $20^{\circ}\text{C}/\text{min}$, from 0 – 230°C . Due to the high sensitivity of the polymer to hydrolytic degradation, experiments have been performed on strictly dried samples in a dry nitrogen atmosphere. Thermal

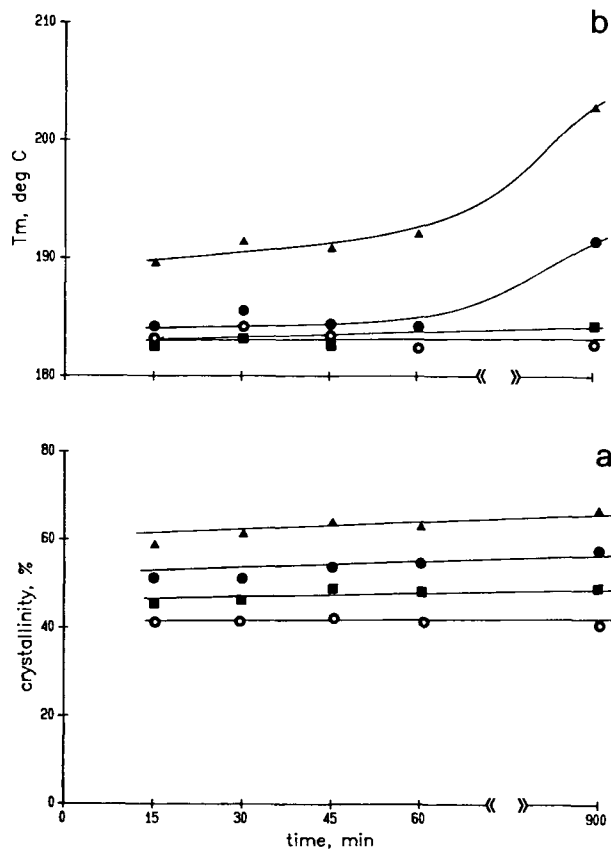


Figure 3 (a) Crystallinity degree and (b) melting temperature of PLA200 as a function of the duration of thermal treatment at (\circ) 100°C , (\blacksquare) 120°C , (\bullet) 140°C , and (\blacktriangle) 160°C .

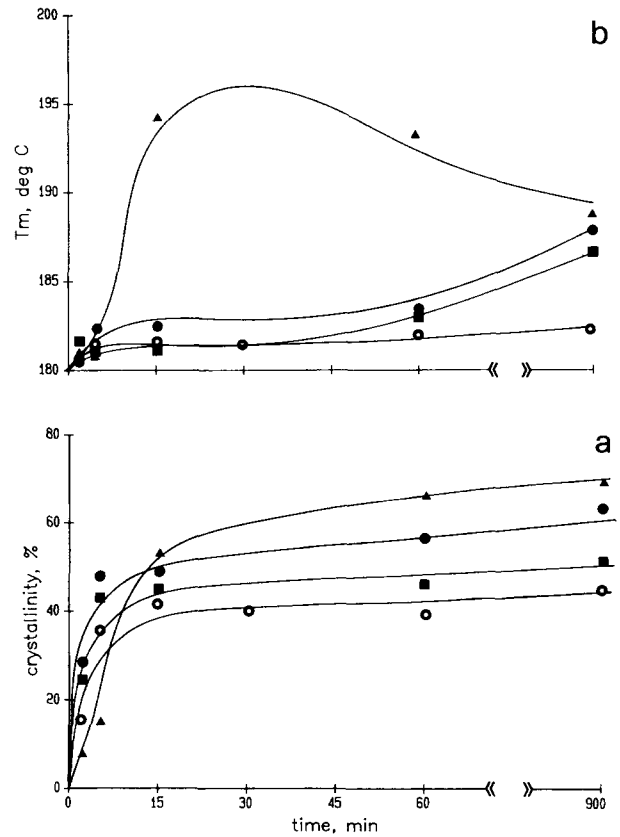


Figure 4 (a) Crystallinity degree and (b) melting temperature of PLA85 as a function of the duration of thermal treatment at (\circ) 100°C , (\blacksquare) 120°C , (\bullet) 140°C , and (\blacktriangle) 160°C .

treatments of samples have been conducted in the differential calorimeter, in the case of small polymer amounts, as well as in an oven with a controlled nitrogen atmosphere for larger materials. DSC scannings performed on the differently treated materials showed no appreciable differences.

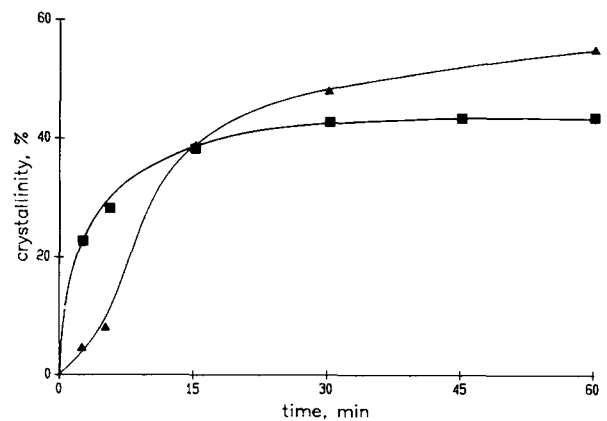


Figure 5 Crystallinity vs. treatment time of PLA230 annealed at 120°C (\blacksquare) and 160°C (\blacktriangle).

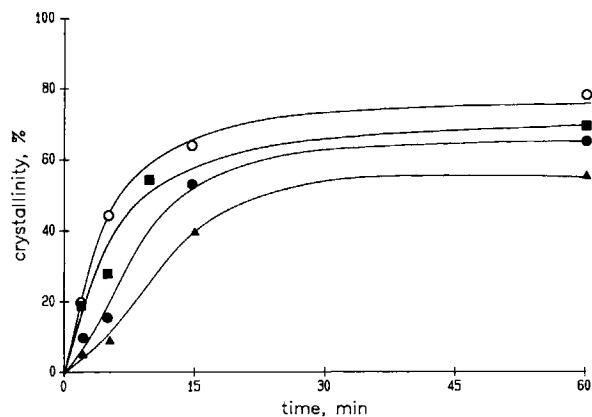


Figure 6 Crystallinity vs. treatment time at 160°C of PLA230 (▲), PLA85 (●), PLA68 (■), and PLA40 (○).

Molecular weight determinations were made by means of viscosimetric measurements of diluted chloroform/polymer solutions in a Ubbelohde viscosimeter at 25°C. The viscosimetric molecular weight, M_{wv} , was calculated from the intrinsic viscosity by using the following equation²⁴:

$$[\eta] = 5.45 \times 10^{-4} \times M_{wv}^{0.73}$$

Dynamic mechanical tests were conducted under a bending loading mode in a dynamic mechanical thermal analyzer (DMTA, model MKII), by Polymer Laboratories, at a frequency of 1 Hz, from 30–150°C with a heating rate of 2°C/min.

RESULTS AND DISCUSSION

In an attempt to bring all samples to the same initial amorphous state, the different materials were quenched from the melt to room temperature. Figure 1 presents a typical thermogram, in this case for PLLA with molecular weight equal to 85,000, demonstrating the effectiveness of the quenching procedure. The amorphous nature of the material is revealed by the fact that the crystallization exotherm and melting endotherm have identical energy content (the same area). Clearly, the 22% relative crystallinity of the material developed at a relatively high temperature range starting at around 95°C. Above the glass transition, PLLA chains have sufficient thermal energy to rearrange and develop crystalline arrays. The sharp glass transition is consistent with

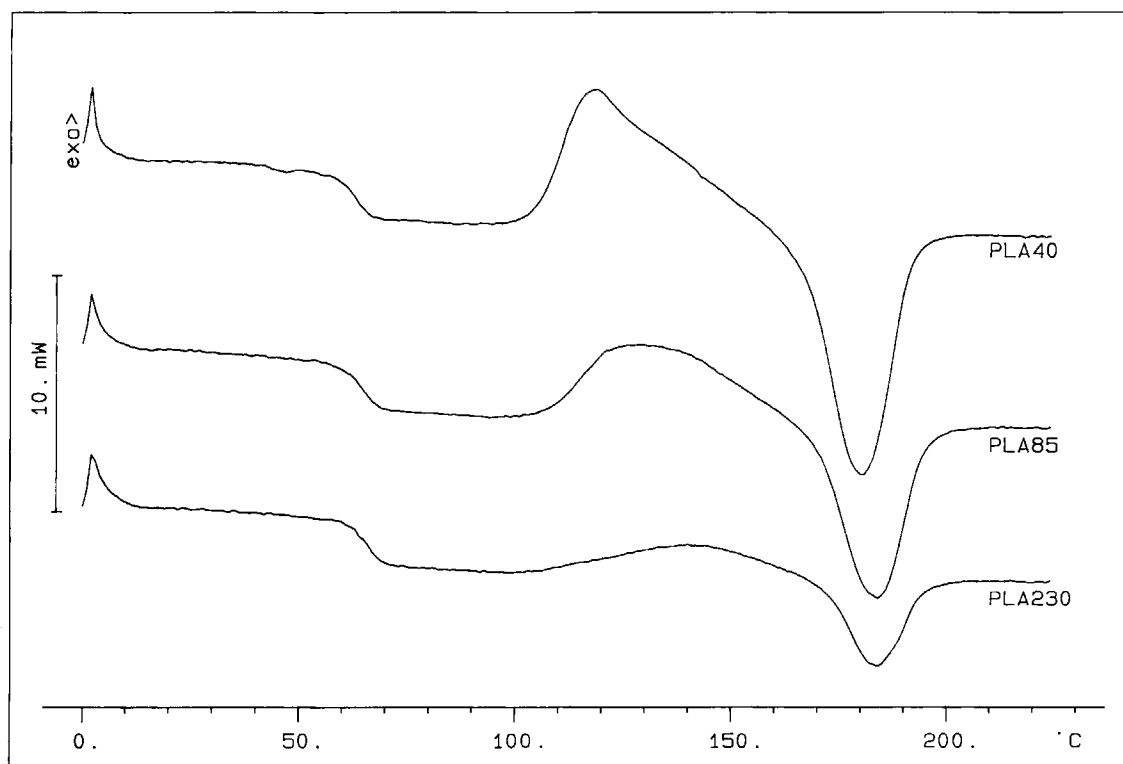


Figure 7 DSC thermograms for PLLA of three different molecular weights as indicated. Samples were of identical weight.

the fully amorphous state of the PLLA starting material.

The molecular weight of the molded specimens was determined and compared to that of the corresponding as received material. The data presented in Table I clearly show that significant thermal degradation has taken place, even though precautions were taken and the materials were thoroughly dried.

Significantly lower molecular weights were measured also for samples after different thermal treatments, conducted in an oven, in a nitrogen atmosphere, under strictly controlled dry conditions. This is exemplified in Table II, which shows the extent of chain scission as a function of time at $T = 160^\circ\text{C}$, i.e., the highest used curing temperature, for two PLLA samples that represent the extremes of the molecular weight range being studied.

Additional experiments, conducted in the DSC apparatus under dry nitrogen, after repeated flushing and purging, using thoroughly dried material, showed similar results.

It becomes apparent, therefore, that the degradation is caused by the thermal cleavage of the macromolecules, not by a hydrolytic process. Depending on the temperature and on the treatment duration, degradation of PLLA appears to be an unavoidable effect that must be taken into consideration while defining the material processing and annealing conditions.

Figure 2 presents combined crystallinity and molecular weight data for PLA230 specimens (initial $M_w = 230,000$) undergoing thermal treatments at 160°C , for different periods of time, and then quenched. The crystallinity degree vs. treatment

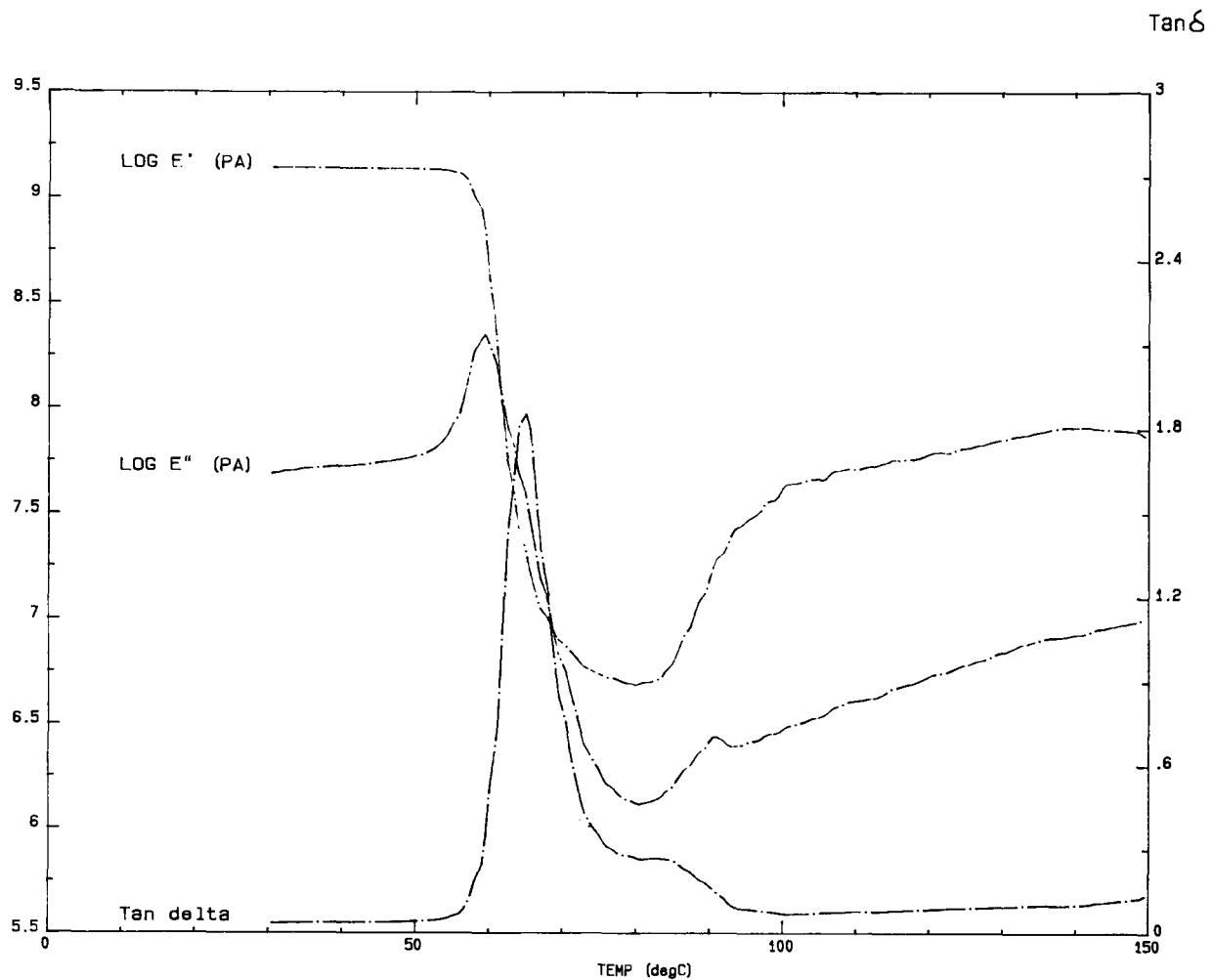


Figure 8 Storage (E') and loss (E'') moduli and damping ($\tan \delta$) measured at 1 Hz as a function of time for amorphous PLA40.

time curve displays a fast initial increase followed by a much slower raise, attaining an 89% level after 90 h. Given the high treatment temperature (approximately 100°C above the glass transition), the amorphous material develops very rapidly its crystallizability; however, as crystallinity develops, molecular motion is increasingly hindered, resulting in the slowing down effect just described. Already after 15 min, PLLA displays a sharp melting endotherm at 189.5°C, shifted to 191.9°C after 1 h. These findings indicate that the increase in the degree of crystallinity (see Fig. 2) is accompanied by the development of better organized crystallites. It should be stressed, however, that the temperatures reported are shifted to somewhat higher values due to the rather fast heating rate used (20°C/min). Separate experiments conducted at slower heating rates (10, 5, and 1°C/min) displayed the expected shift to

somewhat lower temperatures, while the basic pattern of the phenomena under study remained unchanged.

Simultaneously, a steady decrease of the molecular weight as crystallization proceeds was detected, this not necessarily implying that a causative relation exists between the two phenomena. Moreover, the plateau region in Figure 2 seems to indicate that the degree of crystallinity of the sample is independent of its molecular weight. However, when the chain length becomes shorter than a critical minimum value, the increasing defect concentration due to the chain ends will play a determinant role, interfering with the development of crystalline arrays. Nevertheless, for higher molecular weights, the influence of the chain ends becomes negligible, the equilibrium degree of crystallinity being now essentially independent of the chain length. It should be

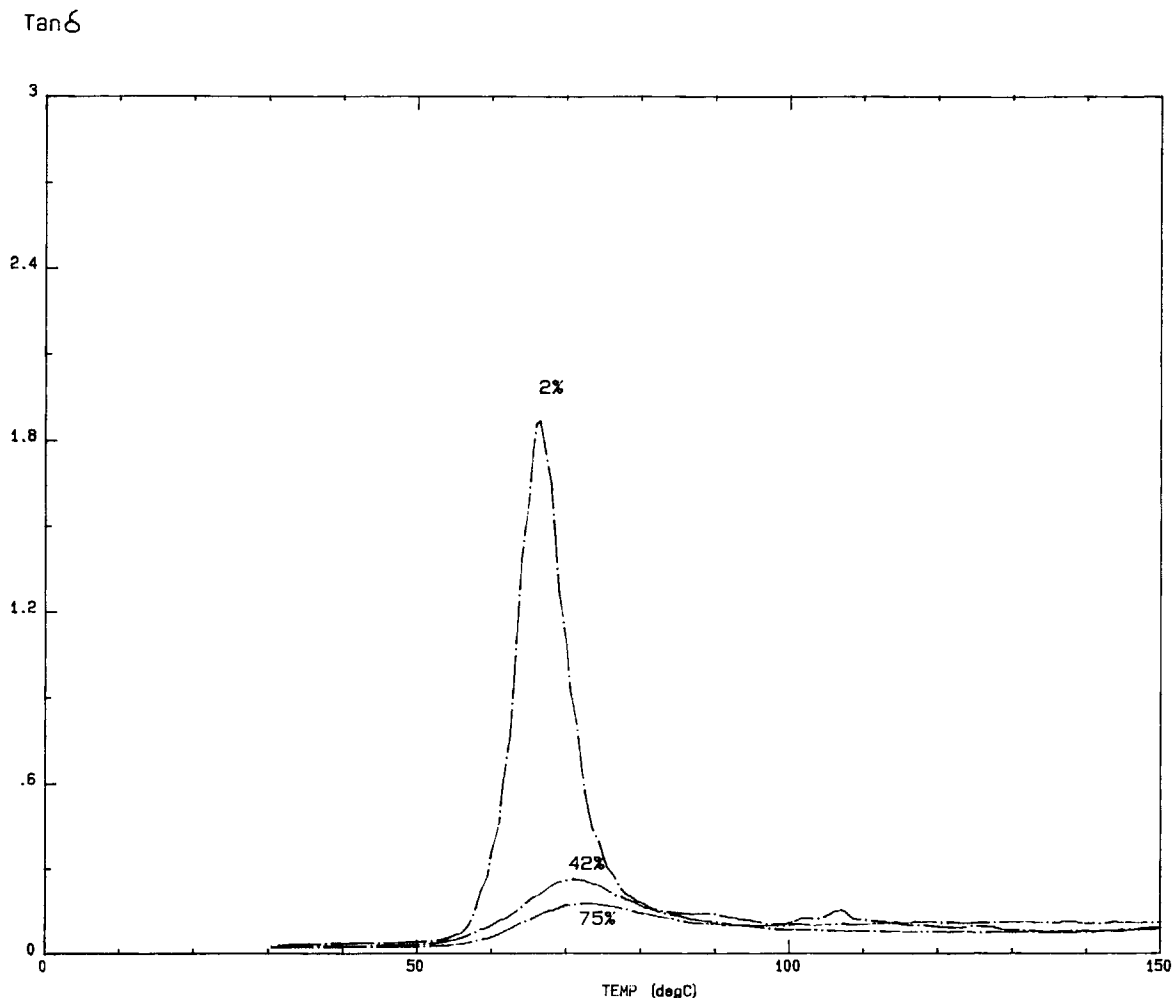


Figure 9 Effect of the crystallinity on damping of (a) PLA85 and (b) PLA230.

stressed, however, that kinetic effects could be an important limiting factor, as chain mobility decreases as molecular weight increases. Therefore, lower crystallinity values could be obtained, within the time scale of the experiments, for high molecular weight PLLA chains.

The effect of the treatment temperature on the rate at which crystallization develops is presented in Figures 3 and 4 for two different molecular weight PLLA matrices. As expected, both the maximum degree of crystallinity attained by the material, as well as the rate at which it increases, are a function of temperature. It can be seen in Figure 3(a) that at the lowest temperatures (100 and 120°C) almost constant crystallinity levels are attained, the plateau being lower the lower the temperature of the treatment. For the higher temperatures (140 and 160°C), no maximum constant value for crystallinity was measured for the duration of the treatment. Cor-

respondingly, the melting temperatures of the materials annealed at the higher temperatures increase as a function of time, as reported in Figure 3(b). The glass transition temperature showed a consistent tendency to increase with the degree of crystallinity, due to the expected stiffening effect of the crystallites on the amorphous phase.

An additional factor to consider has to do with the thermal degradation of the polymer during the treatment, the extent of degradation being a function of the temperature. The findings in Figures 3(a) and (b) can be understood in light of the following considerations. It can be surmised that due to the relatively high molecular weight of the starting polymer (200,000) the shorter chains generated during degradation also fall within the length range for which crystallinity is essentially independent of molecular weight. The data in Figure 2 are fully consistent with this explanation, a plateau level

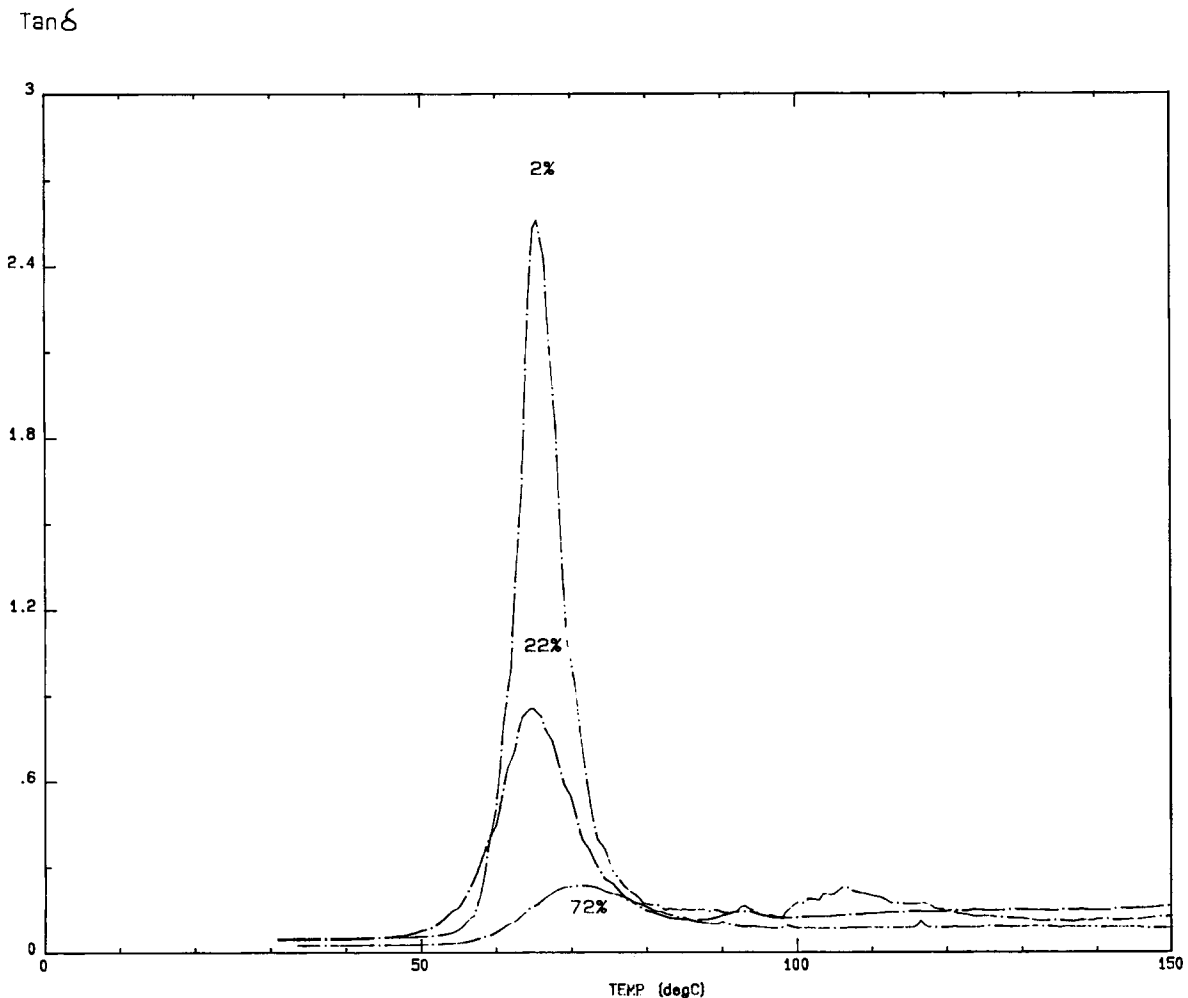


Figure 9 (continued from the previous page)

being apparent even though considerable chain scission is taking place.

The fact that a constant crystallinity level is reached already at the early stages of the experiment, no further increase in crystallinity being gained for longer treatment periods, has rather important applicative implications. Clearly, short treatments should be preferred, not only because longer ones do not result in higher crystallinity values but, most importantly, due to the thermal degradation that inevitably accompanies the treatment. The important consequence of this phenomenon pertains to the detrimental effect of reducing the molecular weight on the mechanical properties of the material, an aspect that will very much determine the biological performance of the implanted system.

PLA samples having different molecular weights exhibited the same thermal behaviour just described. This is exemplified in Figure 4 for an 85,000 PLLA polymer that follows a basic pattern consistent with the previous discussion. In this case, however, where the effect of very short time crystallization treatments has been investigated, at 160°C the initial crystallization rate proceeds slower than at lower treatment temperatures, even if higher crystallinity levels are reached already after 15 min. Crystallization measured as a function of the time for the 230,000 weighing PLLA at 120 and 160°C (see Fig. 5) proceeds similarly, a lower crystallization kinetics and final crystallinity being displayed for the higher temperature treated material. These findings well agree with data reported in ref. 25, where an increase and then a decrease of the crystal radius growth rate with temperature was observed.

The behaviour described is seen as determined by the relation between the temperature of the treatment and both the glass transition of the starting amorphous matrix on one hand and the melting temperature of the increasingly crystalline polymer on the other. Clearly, the higher the working temperature, the more mobile the polymeric chains. This accounts for the initial faster response of the amorphous material because of the larger temperature difference with T_g . However, the higher the treatment temperature, the closer it is to the gradually increasing T_m of the crystallizing polymer. This should explain the observed decrease of the polymer initial crystallization kinetics at 160°C until the melting temperature of the polymer increases as crystallinity develops.

Figure 6 presents crystallinity vs. treatment time curves, at 160°C, for four PLLA samples, characterized by different molecular weights. It is apparent

from the data shown that the polymers display significant differences in both the rate of crystallization increase, as well as the maximum value attained during the treatment. The behaviour encountered can be attributed to the gradually decreasing mobility of the polymeric chains as their molecular weights increase. This, in turn, significantly hinders the possibility of the chain to rearrange in space, therefore kinetically controlling the maximum degree of crystallization attainable. The differences among the different molecular weight polymers do not substantially change with the treatment temperature.

The DSC thermograms shown in Figure 7 clearly demonstrate the pronounced influence that the chain length exerts on the molecular mobility of the different PLLA polymers and, in consequence, their substantially different ability to crystallize. While a relatively low molecular weight ($M_w = 37,000$) amorphous polymer is able to rapidly crystallize during the fast heating cycle (20°C/min), as revealed by the rather sharp crystallization exotherm, this process is hindered for longer chains. This is especially clear for the high molecular weight PLA230 ($M_w = 230,000$), where only a broad and ill-defined exotherm could be detected.

DMTA

The storage modulus E' , the loss modulus E'' , and the damping $\tan \delta$, measured in bending under dynamic loading conditions, are reported in Figure 8 as a function of temperature for an untreated, initially amorphous PLA40 sample.

The glass transition temperature of the polymer is well evident in the sharp decrease of E' following the initial glassy plateau. Due to the corresponding increase of E'' at T_g , as the molecular relaxation takes place, the $\tan \delta$ curve exhibits a well-quoted peak, with a much better overall resolution of the transition phenomenon than in the calorimetric analysis.

Most polymers usually display, after T_g , a second plateau region in the E' curve. The extension of this plateau will depend on the crystallinity and molecular weight of the polymer until the respectively limiting processes of melting or degradation take place. In the case of PLA40 (see Fig. 8), however, the increase in chain mobility of the material above T_g favours the activation of the crystallization process, which proceeds as temperature increases. After a second short plateau following the T_g , the storage

modulus of the polymer significantly increases due to the increase in crystallinity. This process continues until the enhanced crystallinity reduces the molecular mobility and, therefore, the crystallization rate of the polymer. Kinetics becomes slower and further development of crystallinity takes a very long time, at least as compared to the duration of the experiment. This results in a new, apparent plateau, the level of which accounts for the stiffening effect exerted by the crystalline domains on the modulus of the amorphous material.

The different degrees of crystallinity largely affect the height of the $\tan \delta$ peak, as shown in Figures 9(a) and (b), for PLA85 and PLA230, respectively. The height of the damping peaks should account for the differences in the polymer crystallinity, being the transition associated only with the polymer amorphous regions mobility. A quantitative depen-

dence of PLLA crystallinity on the damping value has not been detected, this contrasting with relationships of this kind reported in the literature for other semicrystalline polymers.²⁶

From the position of the peak along the temperature axis, a more precise evaluation of the polymer glass transition temperature can be made. The results, however, obtained from the large number of samples that have been investigated indicated that the T_g scatter significantly as a result of the complex, combined effect of both molecular weight and crystallinity. In the $\tan \delta$ curves, additional, though much smaller, peaks or shoulders are sometimes evident; their correlation with other transition phenomena occurring in the materials, likely associated with conformational changes, appears to be difficult.

The E' vs. T curves for PLA85 samples having different degrees of crystallinity are shown in Figure

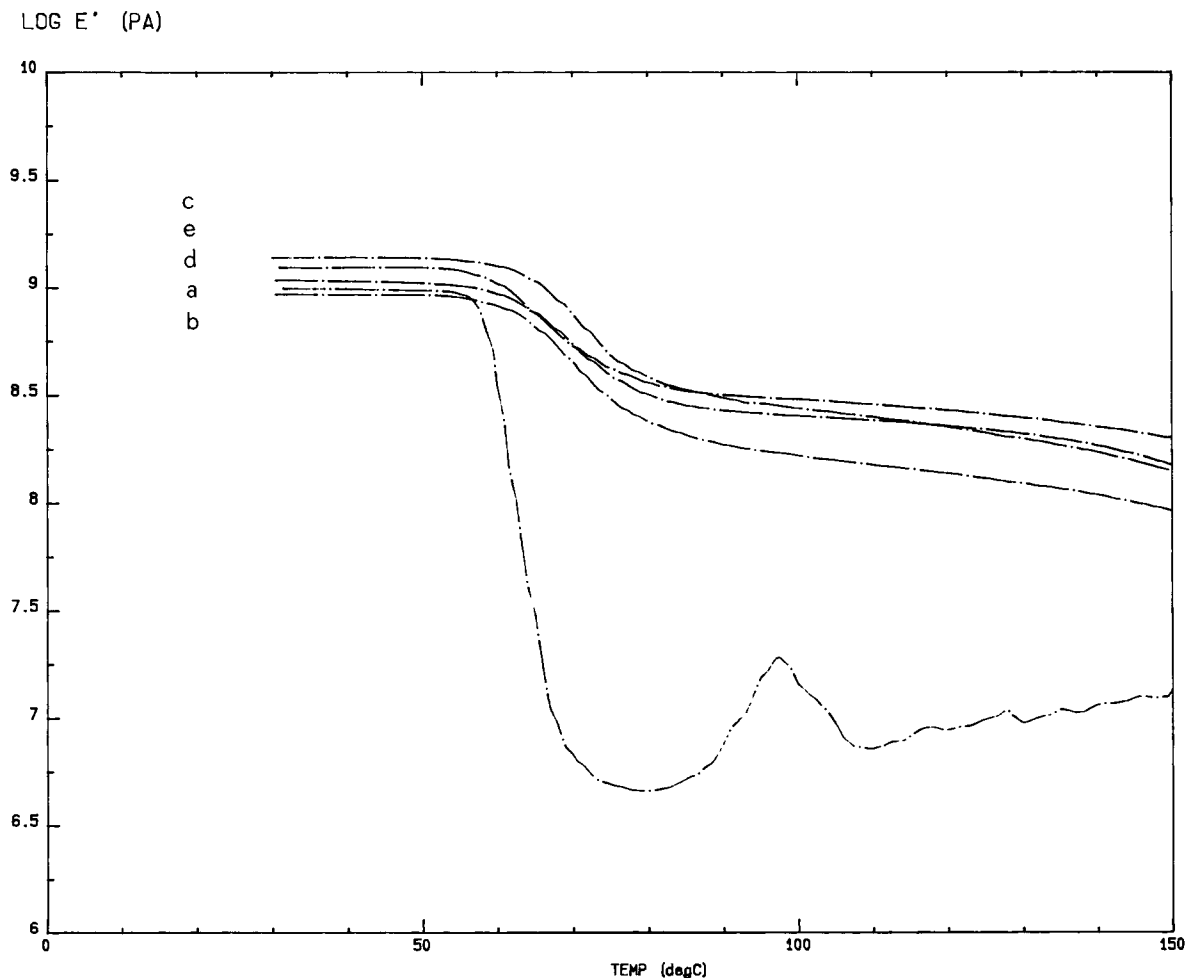


Figure 10 E' vs. temperature of PLA85 with initial crystallinity degree equals to (a) 2, (b) 43, (c) 46, (d) 50, and (e) 53%.

10. The more crystalline polymers do not exhibit any further crystallization process after T_g . These findings are in full agreement with the slower crystallization kinetics displayed by the polymers with initial higher crystallinity. The two typical glassy and rubbery plateau are exhibited with the transition from one mechanical behavior to the other taking place at temperatures that depend on the crystallinity and actual molecular weight of the polymer. It should be stressed, however, that due to softening of the samples as temperature approaches T_m the experimental temperature range was bounded at 150°C. Therefore, the analysis was confined to phenomena taking place at relatively low temperatures, additional crystallization processes being expected at higher temperatures.

Given the same molecular weight, storage moduli should increase with crystallinity. Due to the test settings, the absolute values of the moduli are not

fully reliable, even if data within the same curve can be assumed to be consistent. Accordingly with the above statement, in fact, the differences between the modulus values in the glassy and rubbery state decrease with crystallinity.

The curve of untreated PLA85 differs from that of the previously shown PLA40: After a comparable increase starting at approximately 85°C, the E' value shown by PLA85 decreases once again, with a peak being exhibited in the loss modulus vs. T curve. The same behaviour is presented also by PLA230 curves (see Fig. 11) for the amorphous and 9% crystalline samples, while the behaviour of the more crystalline specimen (22%) is comparable with that of the previously presented amorphous PLA40. Experiments performed on PLA40 samples taken from a different sheet have displayed, however, the presence of a similar peak. Further experiments behave similarly, and indicate that during the test, when the temper-

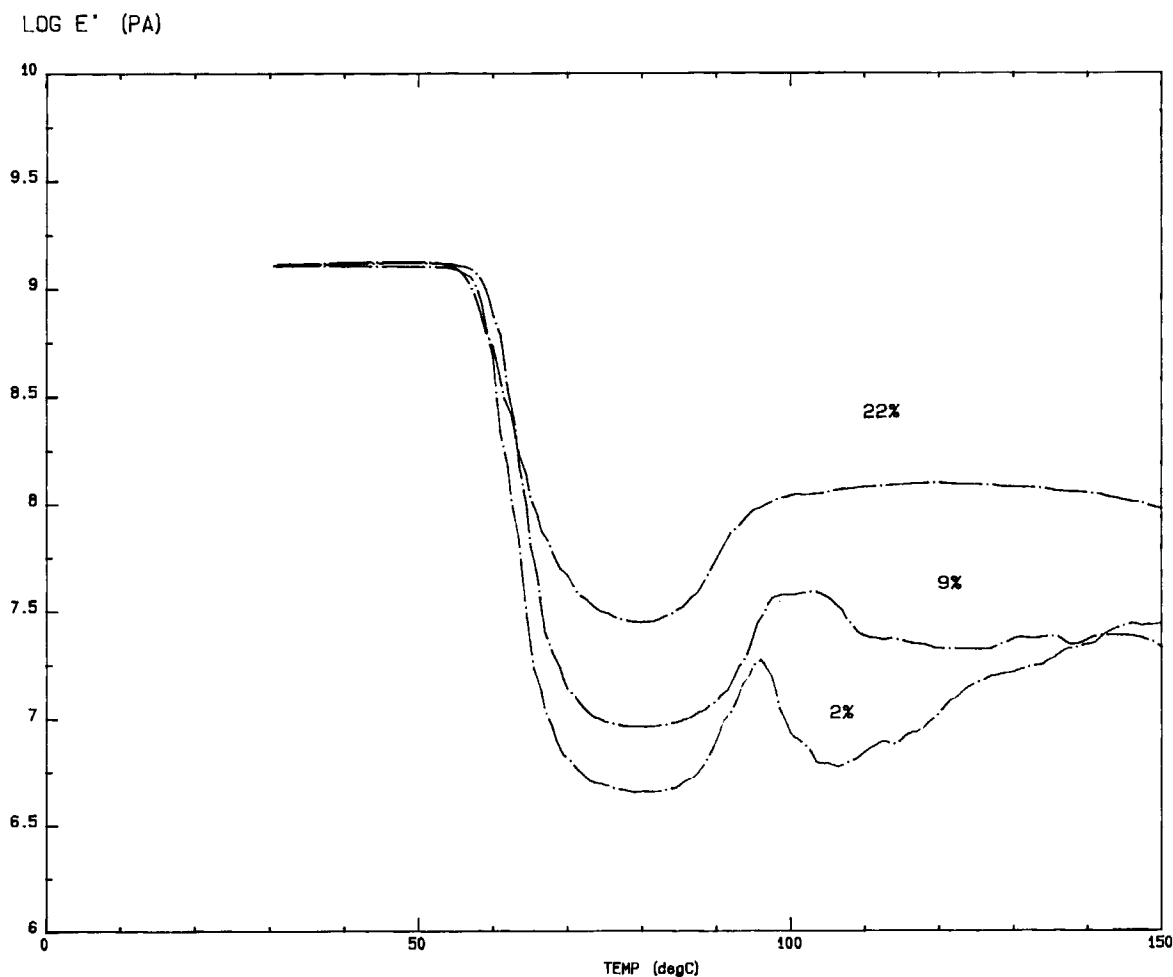


Figure 11 E' vs. temperature of PLA230 at different initial crystallinity as indicated.

ature of 85–90°C is reached, the modulus increases if crystallinity is below a certain value. The phenomenon can be stable or not (i.e., after the raise a decrease of E' can be detected) as function, once again, of the polymer M_w and crystallinity.

Since they were treated at rather low temperatures, the three samples presented in Figure 11 have very similar initial molecular weights while clearly differing in their degrees of crystallinity. This rendered the curves reported, especially useful in assessing the effect of crystallinity on polymer behaviour.

To gain a better insight into these phenomena, four different amorphous samples of PLA40 (taken from a PLLA sheet with molecular weight 37,000) have been run in the DMTA from 30 to 80, 95, 110, and 150°C, respectively, and then suddenly

quenched. In addition to the initial and final temperatures, the three additional points were selected just before, at the peak, and immediately after the increase and subsequent decrease of E' after the sharp drop at T_g . After each run, the glass transition temperature, crystallinity, and molecular weight of the polymer were measured.

The E' vs. T results presented in Figure 12 demonstrate that, while the molecular weight of the sample does not appreciably change during the experiment, a sudden increase of crystallinity occurs 20–30°C after the glass transition, confirming that the increase of the storage modulus after T_g is a result of a crystallization process of the material. As the temperature increases, a progressive but lower additional gain in crystallinity is achieved in full agreement with the overall expected behaviour. The

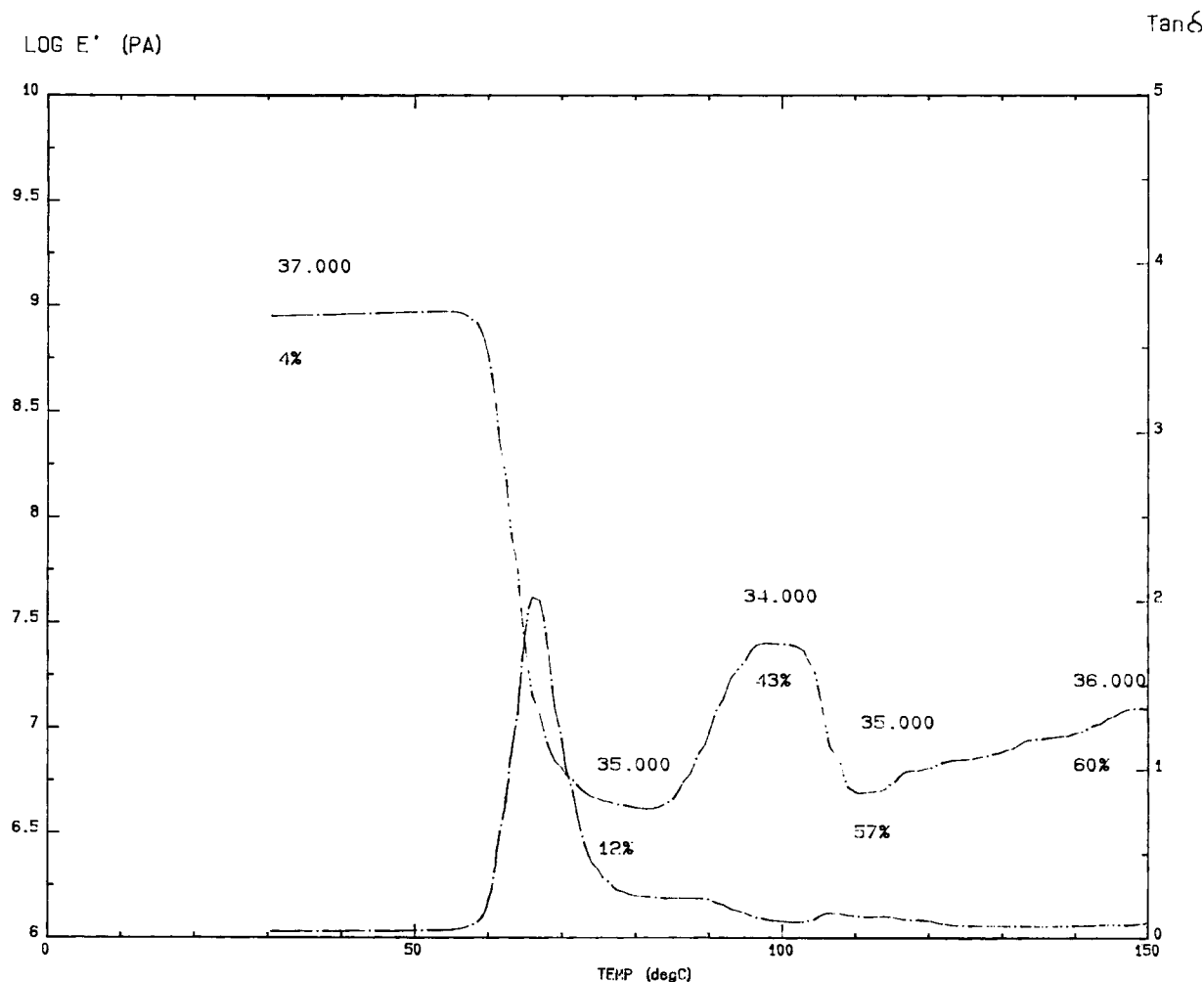


Figure 12 Molecular weights and crystallinities measured on four different PLA40 samples run in the DMTA up to 80, 95, 110, and 150°C. The values reported on the E' and $\tan \delta$ curves indicate how molecular weight and crystallinity change during a 150°C run.

presence of the peak in the storage modulus curve, generated by the decrease in E' , cannot be theoretically accounted for and must therefore be attributed to limits that the apparatus presents when measuring the bending modulus of the softened polymer. In other words, the peak appears to be an artefact due to the test setting and apparatus capability, which could be overcome if the material rigidity after T_g would be higher than a certain value.

In agreement, three different PLA40 samples, similar to the ones presented in Figure 12, have been treated in the DSC with a heating rate of $2^\circ\text{C}/\text{min}$ from 30 to 95, 110, and 150°C , respectively, following partial paths of the run reported in Figure 13(a). Crystallinities, measured from the difference of the areas between the melting and crystallization peaks in the following scan [Figs. 13(b), (c), and (d)], appear to be consistent with those measured for the DMTA-treated samples. The treatment, which in this case has been performed with a heating rate of $2^\circ\text{C}/\text{min}$, leaves the materials enough time to develop crystallinity even at lower temperatures, as shown by the fact that only a residual small crystallization develops in the next DCS full scan [Fig.

13(b)]. In this case, another small crystallization peak appears just before the melting, which has been detected, independently on the heating rate, for samples with a certain initial crystallinity range. This peak can be associated with secondary crystallizations and is argument of work in progress.

CONCLUSION

The results have shown the need for an accurate definition of the conditions of both processing and annealing, being molecular weight and crystallinity and, hence, the material properties dependent on time and temperature of treatment.

Very high crystallization degrees can be attained by the combined effect of time and temperature of annealing; nevertheless, the process is always associated with a thermal cleavage that causes a substantial reduction in the polymer molecular weight. Independently of the initial molecular weight and of the temperature of annealing, crystallization proceeds at the beginning with a very fast kinetics, reaching a quasi equilibrium value. Further crystal-

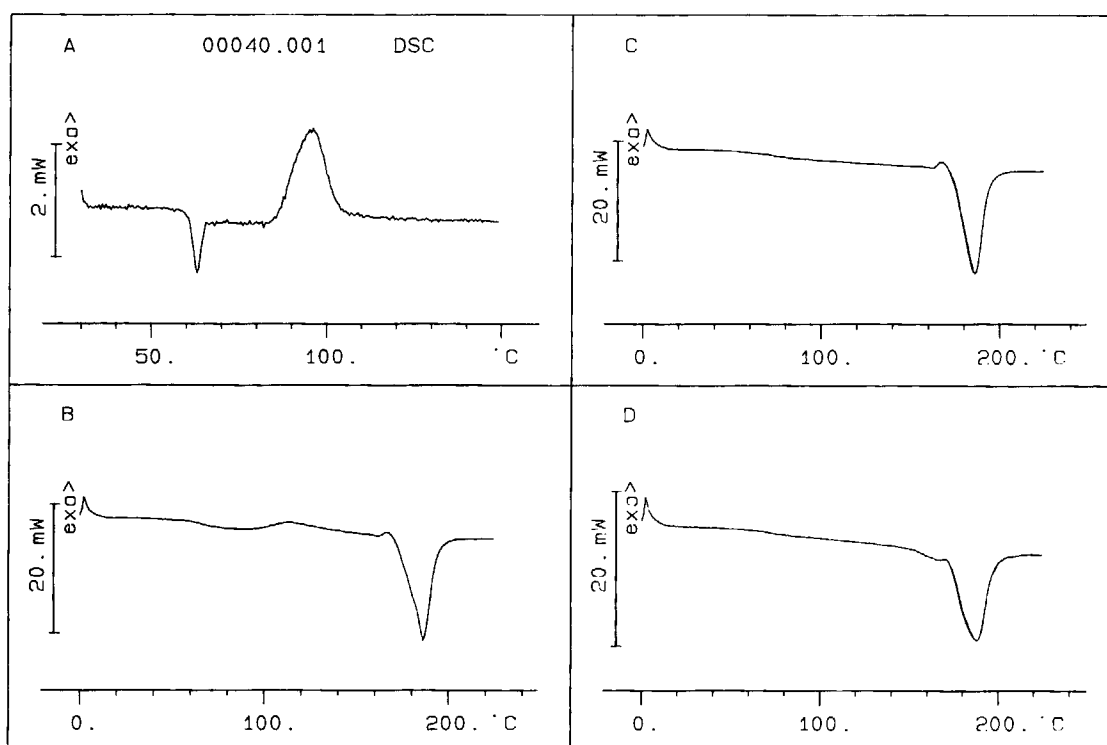


Figure 13 DSC thermograms for (A) amorphous PLA40 and samples treated in the DSC up to (B) 95, (C) 110, and (D) 150°C .

lization is developed after very long treatments, but at the expense, however, of the polymer molecular weight.

Less amorphous materials have a lower damping and, consistent with the previous findings, a lower crystallization capability, as shown by the samples during the DMTA runs.

REFERENCES

1. D. K. Gilding, in *Biocompatibility of Clinical Implant Materials*, D. F. Williams, Ed., CRC Press, Boca Raton, FL, 1982, pp. 209-232.
2. T. H. Barrows, *Clin. Mater.*, **1**, 233-257 (1986).
3. R. K. Kulkarni, K. C. Pani, C. Neuman, and F. Leonard, *Arch. Surg.*, **93**, 839-843 (1966).
4. R. K. Kulkarni, E. G. Moore, A. F. Heygell, and F. Leonard, *J. Biomed. Mater. Res.*, **5**, 169-181 (1971).
5. A. K. Schneider (Ethicon), U.S. Patent 3,636,956 (1972).
6. W. H. Carothers, G. L. Dorough, and F. J. van Natta, *J. Am. Chem. Soc.*, **54**, 761 (1932).
7. A. R. Katz and B. J. Turner, *Surg. Gynecol. Obstet.*, **131**, 701 (1970).
8. E. E. Schmitt, U.S. Patent 3,297,033 (1967).
9. O. Aydin and R. C. Schulz, *Makromol. Syn.*, **8**, 99 (1982).
10. J. M. Brady, D. E. Cutright, R. A. Miller, G. C. Battistone, and E. E. Hunsuck, *J. Biomed. Mater. Res.*, **7**, 155-166 (1973).
11. A. S. Chawla and T. M. S. Chang, *Biomater., Med. Dev., Art. Org.*, **13** (3&4), 153 (1985-86).
12. J. W. Leenslag, S. Gogolewski, and A. J. Pennings, *J. Appl. Polym. Sci.*, **29**, 2829-2842 (1984).
13. J. W. Leenslag, A. J. Pennings, R. R. M. Bos, F. R. Rozema, and G. Boering, *Biomaterials*, **8**, 311 (1987).
14. T. Nakamura, S. Hitomi, S. Watanabe, K. Jamshidi, S.-H. Jamshidi, S.-H. Hyron, and Y. Ikada, *J. Biomed. Mater. Res.*, **23**, 1115 (1989).
15. M. Vert, P. Christel, H. Garreau, M. Audion, M. Chavanaz, and F. Chabot, in *Polymers in Medicine II: Biomedical and Pharmaceutical Applications*, E. Chiellini, P. Giusti, C. Migliaresi, and L. Nicolais, Eds., Plenum Press, New York, 1986, pp. 263-275.
16. M. Vert and F. Chabot, *Makromol. Chem.*, **5**, 30 (1981).
17. D. C. Tunc, *Trans. Soc. Biomater.*, **6**, 47 (1983).
18. T. M. Jakanicz, H. A. Nash, D. L. Wise, and J. B. Gregory, *Contraception*, **8**, 227 (1973).
19. L. R. Beck, D. R. Cowsar, D. H. Lewis, R. J. Coxgrove, C. T. Riddle, S. L. Lowry, and T. Epperly, *Fert. Ster.*, **31**, 545 (1979).
20. E. Nyilas, T. H. Chiu, J. M. Hegarty, L. A. Trudell, and P. M. Galletti, *Conference Abstracts of the 9th Annual Meeting of the Society for Biomaterials*, Birmingham, AL, April 27-May 1, 1983, p. 84.
21. D. C. Tunc, M. W. Rohovsky, and B. Jadhav, in *Advances in Biomedical Polymers*, G. Gebelein, Ed., Plenum Press, New York, 1987, pp. 87-99.
22. J. W. Leenslag and A. J. Pennings, *Makromol. Chem.*, **188**, 1809 (1987).
23. B. Eling, S. Gogolewski, and J. A. Pennings, *Polymer*, **23**, 1587-1593 (1982).
24. A. Schindler and D. Harper, *J. Polym. Sci.*, **17**, 2593-2599 (1979).
25. R. Vasanthakumari and A. J. Pennings, *Polymer*, **24**, 175-178 (1983).
26. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974, vol. I.

Received March 26, 1990

Accepted October 16, 1990