

# Amorphous and crystalline morphologies in glycolic acid and lactic acid polymers

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This paper describes an investigation of a number of parameters which affect the physical structures of glycolic acid (GA) and lactic acid (LA). It has been found that the cooling rate of a quenching process determines the amorphous-crystalline morphology balance, and that the effect of a similar quenching process will vary with the molecular weight of the polymer. At very high molecular weights, even very rapid quenching does not produce higher degrees of amorphous phase. Copolymerization of PGA or of PLA with poly(ethylene oxide) results in either phase blending or phase separation, depending on the copolymer composition and the segmental chain length. The degree of crystallinity of the PGA or PLA component in the copolymer is mostly affected by copolymerization in a state of phase blending.

(Keywords: poly(glycolic acid); poly(lactic acid); poly(ethylene oxide); biodegradable polymers)

## INTRODUCTION

Poly(glycolic acid) (PGA) and poly(lactic acid) (PLA) are well established as very useful biodegradable polymers, covering a wide range of applications, such as dental, orthopaedic and drug delivery<sup>1-7</sup> which have emerged from the original suture development<sup>8-10</sup>. The scientific literature offers a vast amount of data and information on these polymers, and readers may refer to reviews<sup>11-12</sup>.

A particular aspect which seems to have been rather neglected in the literature is the morphological structure of these materials. PGA and PLA appear with different degrees of crystallinity, from completely amorphous to a maximum of 52% crystallinity in the PGA and of 37% in the poly(L-lactic acid), while poly(DL-lactic acid) is always amorphous<sup>13</sup>.

The practical significance of the variable crystallinity has been discussed by Gilding and Reed<sup>13</sup>. They pointed out that the amorphous state is ideal for applications where it is necessary to have mass loss simultaneously with molecular weight degradation, or for applications such as drug delivery, where it is important to have a homogeneous dispersion of the active species in a monophasic matrix. The partially crystalline morphology is relevant to uses where high mechanical properties are required, i.e. in sutures and in orthopaedic or dental applications. In addition to these examples, it is expected that the degree of crystallinity will influence chemical and physical properties, such as swelling behaviour and the hydrolytic sensitivity of these polymers and, consequently, their rate of biodegradation.

Gilding and Reed also showed<sup>13</sup> that the degree of crystallinity in cast polymer films was controllable by copolymerization of GA with LA at different compositions, with those of 22-66 wt% GA being fully amorphous. They also found that quenching of copolymer compositions, which were potentially to produce partially crystalline morphologies, resulted in amorphous polymers. However, when these polymers

were implanted in the physiological environment or placed in water, they crystallized partially over 24-72 h, hence it was impossible to retain quenched morphologies under those conditions.

The present study investigated further a number of parameters that may potentially control the amorphous/crystalline morphologies in glycolic acid and lactic acid polymers. These parameters are the rate of quenching, the molecular weight of the polymer and copolymerization of GA or LA with poly(ethylene oxide), parameters which are known to substantially affect the morphology developed by polymeric matrices.

## EXPERIMENTAL

### Materials

PGA and PLA with high molecular weight ( $MW > 20\,000$ ) were obtained from Polysciences, Inc. The low molecular weight samples ( $MW \leq 10\,000$ ) were prepared in our laboratory by simple polycondensation reactions using glycolic acid (Fluka) and a 90% solution of (L<sup>+</sup>) lactic acid (Merck); poly(ethylene oxide) with different molecular weights were obtained from Aldrich. The  $Sb_2O_3$  catalyst was supplied by Fluka.

### Analytical methods

**Carboxylic end-group analysis.** Samples of PLA with different molecular weights were dissolved in approximately 20 ml of a 1:1 solution of benzyl alcohol (Merk, Analar grade) and chloroform (Frutarom, Analar grade) and titrated against 0.05 M KOH in benzyl alcohol solution in the presence of phenolphthalein indicator. The number of COOH end groups present in each polymer sample was calculated and the molecular weight ( $M_n$ ) determined.

**Thermal analysis.** A Mettler TA3000 differential scanning calorimeter (d.s.c.) calibrated with indium was used to determine the glass transition ( $T_g$ ), the melting

( $T_m$ ) and crystallization ( $T_c$ ) temperatures and the heat of fusion ( $H_f$ ) of the various materials investigated. Three different cooling rates were used: fast cooling ( $60^\circ\text{C min}^{-1}$ ), medium ( $20^\circ\text{C min}^{-1}$ ) and slow cooling ( $10^\circ\text{C min}^{-1}$ ). When not stated, the slowest cooling rate was used.

$T_g$  was obtained from the thermograms, using the middle point between the intersections of the two parallel baselines, before and after  $T_g$ , and the d.s.c. trace.  $T_m$  and  $T_c$  were determined as the intersection of the baseline and the edge of the fusion peak. The heat of fusion was estimated from the area enclosed by the d.s.c. curve and the baseline.

All samples were heated (in nitrogen atmosphere) to  $20$ – $30^\circ\text{C}$  above the melting point of the polymer for  $\approx 10$  min to ensure that no trace of crystallinity remained. The melted samples were then cooled at three different rates,  $60$ ,  $20$  and  $10^\circ\text{C min}^{-1}$ , to the desired temperature, which was about  $50^\circ\text{C}$  below the  $T_g$ .

## RESULTS AND DISCUSSION

### PGA and PLA homopolymers

Figure 1 presents a typical d.s.c. trace of high molecular weight (HMW) PGA. The main feature is a melting endotherm at  $222^\circ\text{C}$ , while a small glass transition is present at  $45^\circ\text{C}$ . This thermogram is indicative of a substantially crystalline material, and is in full agreement with the results of Gilding and Reed<sup>13</sup>.

Figure 2 shows the d.s.c. traces during reheating and after a heating-cooling cycle for a medium molecular weight (MMW) PGA, at three different cooling rates. Table 1 summarizes the main data obtained from the results in Figure 2. The clear and relatively sharp glass transition exhibited by the quenched samples and the large crystallization exotherms are indicative of a polymer that contains a large amorphous phase. The increasingly important crystalline character of PGA samples which underwent slower cooling cycles is evidenced by the pronounced decrease of both features. When the molten PGA is cooled rapidly to below  $0^\circ\text{C}$ , the crystallization process is hindered, and an amorphous morphology is frozen in. Upon reheating, the amorphous phase will recrystallize at a typical temperature,  $T_c$ , above  $T_g$ . In fact, two recrystallization points are evident, one around  $90^\circ\text{C}$ ,  $T_{c1}$ , and another in the  $160$ – $180^\circ\text{C}$  range,  $T_{c2}$ . The proportion of the amorphous phase strongly depends on the cooling rate and, for a maximum

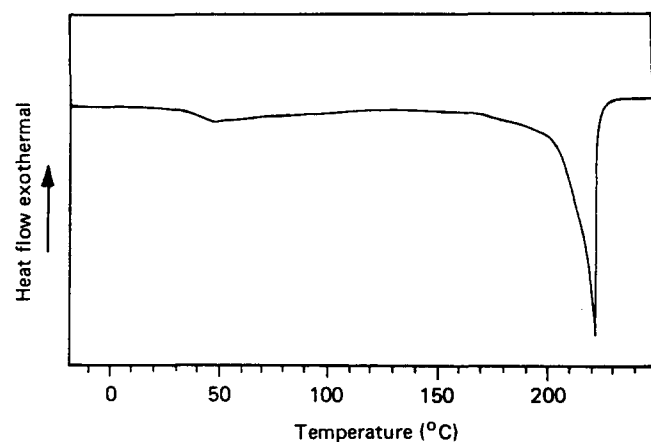


Figure 1 D.s.c. thermogram of HMW PGA

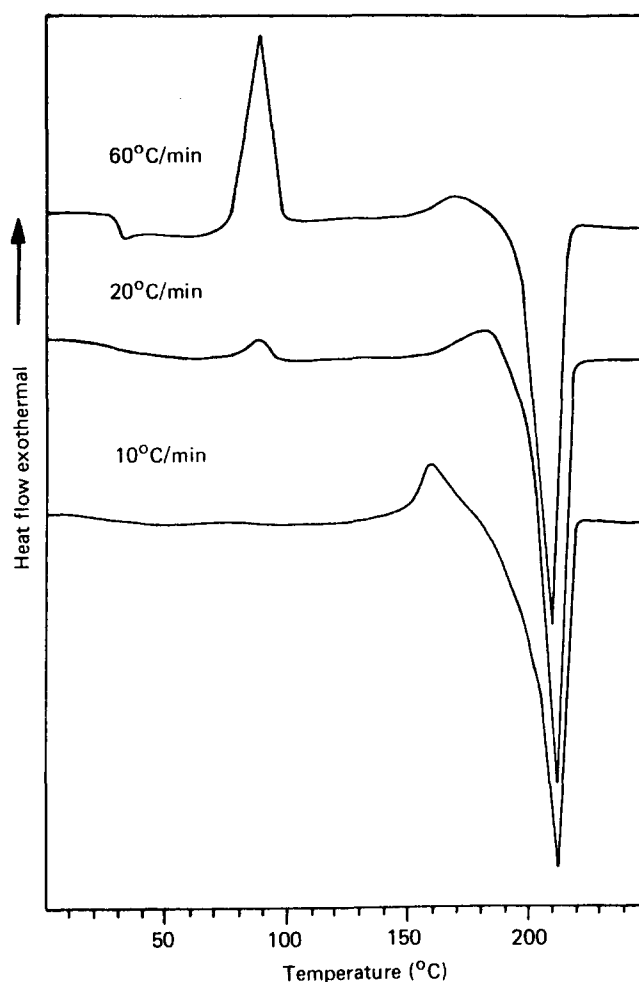


Figure 2 Effect of cooling rate on PGA's thermal behaviour

Table 1 D.s.c. data of MMW PGA

Cooling rate ( $^\circ\text{C min}^{-1}$ )	Temperature ( $^\circ\text{C}$ )				$H_f$ ( $\text{J g}^{-1}$ )	$X_c$ (%)
	$T_g$	$T_{c1}$	$T_{c2}$	$T_m$		
60	30	89	170	208	18.6	13.4
20	31	89	180	212	20.1	14.5
10	—	—	158	213	22.7	16.3

proportion, a quenching rate faster than  $60^\circ\text{C min}^{-1}$  is required, as shown by the large exotherm, which is still present at  $212^\circ\text{C}$ . The final degree of crystallinity,  $X_c$ , was calculated from the heat of fusion,  $H_f$ , compared with the  $72.3 \text{ J g}^{-1}$  value, measured for HMW PGA of maximum 52% crystallinity. Our findings show that  $X_c$  increases slightly, from 13.4 to 16.3%, as the cooling rate decreases from 60 to  $10^\circ\text{C min}^{-1}$ . As one would expect, the melting endotherms are only marginally affected by the cooling procedure, no significant shift or increase in the peaks being evident. This is due to the fact that much of the effect of the cooling rate on the morphology of the sample is eliminated during the reheating cycle; once the system approaches the melting temperature and various crystallization phenomena have already taken place, much of its thermal history has been erased. Still, the trend in  $X_c$  results from the fact that reheating at  $10^\circ\text{C min}^{-1}$  in the d.s.c. experiment does not allow sufficient time for full crystallization. Finally, at this state the origin of the separate  $T_{c1}$  and  $T_{c2}$  crystallizations is still unclear.

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