Melt temperature effects on the polymorphic behaviour of melt-crystallized polypivalolactone

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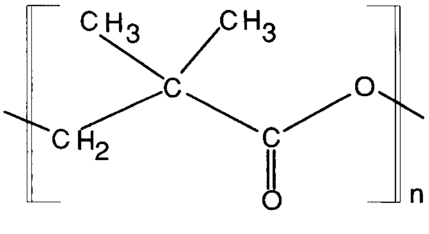
Experimental evidence is discussed indicating that in the case of polypivalolactone (PPVL), the time spent in the melt, and the melt temperature from which the samples are quenched to the crystallization temperature, both affect the subsequent crystallization process, and specifically the relative proportions of the α- and γ-modifications. Neither thermal degradation nor heterogeneous nucleation by extraneous substances appear to account fully for the observed phenomena. The results suggest that the surprising features of the polymorphic behaviour of PPVL, as reported, may relate to the persistence of structural organization, the most likely being nuclei of different crystalline forms, at a temperature which is more than 40°C above the phenomenological melting point, i.e. at temperatures comparable to the proposed equilibrium melting temperature of α-PPVL.

(Keywords: polypivalolactone; polymorphism; melt crystallization)

INTRODUCTION

Previous morphological investigations[1–5] suggested that polypivalolactone (PPVL, see *Scheme 1*) represents a very interesting material for polymer crystallization studies, in particular as a consequence of its very high crystallinity[1–8], as well as the adequate characterization of its crystalline modifications. Polypivalolactone displays three crystalline polymorphs[6,7]: while the β-modification[7,9] is stable only under elongational stress and presents a fully extended conformation, the 'normal' α-phase[6–14] and the γ-phase[1,2,6,7,15] display the typical (-TTGG-)$_2$ twofold-helical structure of poly(β-propiolactone)s[11–13]. These last two polymorphs have a similar packing energy[13] and can be obtained in vastly different proportions upon crystallization from the melt[7]: while exclusive γ-crystallinity has never been reported for macroscopic samples, predominant γ-phase crystallization can be achieved in specimens quenched from the melt to a temperature window which roughly spans the region from 100 to 170°C[1,2,4,5,7,15]. Very high or very low cooling rates, or crystallization temperatures outside this range, yield predominant or exclusive α-phase crystallinity[3,16].



Scheme 1

In this present work we will show that the ratio between the amounts of the α- and γ-modification is also substantially influenced by the time spent in the melt, by the melt temperature from which the quenching is performed, and to some extent, by the previous thermal history.

A number of reports with similar implications, concerning other polymers, have previously appeared in the literature, indicating that the maximum melt or solution temperature can be, at least under certain circumstances, critical in determining the particular crystal modification that is obtained. We recall among others the cases of isotactic polypropylene[17], poly(1-butene)[18], poly(4-methyl-1-pentene)[19] and syndiotactic polystyrene[20]. Whereas self-nucleation effects are taken into consideration at least in the more recent papers, some authors suggest different explanations, probably because the temperatures under consideration are often substantially higher than either the dissolution temperature for solution crystallization or the phenomenological melting point for melt-crystallized material.

EXPERIMENTAL

The sample used in this study has been, unless otherwise indicated, a previously characterized polypivalolactone sample[14,15]. This specimen displayed in all relevant respects the same thermal behaviour as has been described in refs 1–3, 14–16, 21 and 22. Some experiments were also repeated with a specimen obtained from Polysciences, with a viscosity-average molecular weight (M_v) ~ 250 000. Conditions that maximize the γ-phase content in our first sample also had the same effect with the commercial sample. However, contrary to what has been reported elsewhere[1,2,7,15], and also to what we have

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found for our first sample, the Polyscience specimen never gave predominant γ-crystallinity, and even in optimal circumstances the maximum γ/α ratio that was achieved was never above 0.3.

Differential scanning calorimetry (d.s.c.) runs were performed under N_2 by using Perkin–Elmer DSC-2 and DSC-7 instruments equipped with a liquid N_2 cooling device (CCA7); typical sample weights were ~0.002 g. X-ray diffraction measurements were performed, using CuKα radiation, on a Kiessig flat-plate camera and on a Siemens D500 diffractometer, equipped with an automated temperature control system in a N_2 atmosphere.

RESULTS AND DISCUSSION

The d.s.c. traces presented in *Figure 1* are heating curves for different samples after the first melting at different temperatures (T_H) and quenching at a rate of 125°C min^{-1} to 130°C, where samples were allowed to complete their crystallization. *Scheme 2* (full lines) shows the typical thermal cycle used in the present instance: all specimens were first conditioned for 3 min (t_L) at 130°C (T_L); the hold time t_H at the melt temperature T_H, the hold time t_{L1} at 130°C (T_{L1}) and the heating rate in both heating scans, were in all cases, 5 min, 3 min, and 20°C min^{-1}, respectively. With different heating rates, namely 10 and 40°C min^{-1}, similar results were still obtained. The first heating cycle was identical for all of the samples, except for the final temperature (T_H) and this is also displayed in *Figure 1*. Consistent with X-ray diffraction studies, which indicate that the raw polymer is essentially a pure α-modification (see *Figure 2*), it shows a single broad melting endotherm at 234°C (onset at ~228°C), which is characteristic of this PPVL polymorph[8,9]. The second heating cycles (see *Figure 1*), on the contrary, vary widely: those pertaining to specimens brought to melt temperatures T_H of 240 and 290°C display again a single melting peak, which in both cases is close to 230°C, and are again representative of pure α-phase materials. On the other hand, specimens heated to T_H temperatures between ~250 and 280°C show in the second heating cycle two distinct endotherms at ~220 and 234°C, which, consistent with previous literature reports[1,2,7,15] and with our own X-ray evidence (see *Figure 3*), pertain, respectively, to the γ- and α-modifications. With T_H ~250°C, the γ/α ratio, as estimated from the ratio of the two melting endotherms, and qualitatively from X-ray diffractometer scans, is at a maximum (~3), and then diminishes to reach values <0.1 at 270°C. For samples crystallized from T_H values of 280°C, i.e. 10°C above the experimentally determined equilibrium melting temperature[20,21] the γ-form melting endotherm is still discernible, while this is hardly the case for T_H values $\geqslant$290°C. It should be noted that, under the described experimental conditions, the temperature of the α-phase melting transition

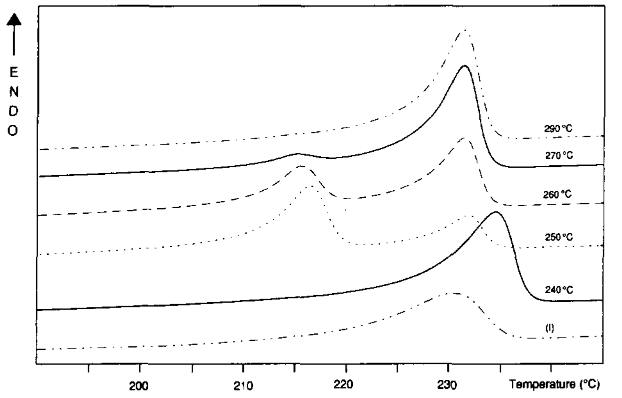
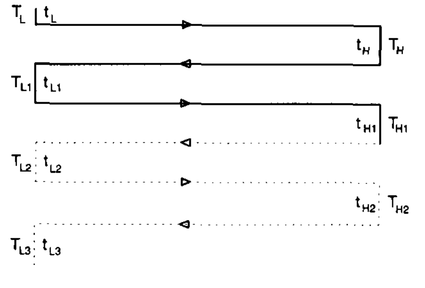


Figure 1 Melting behaviour of different PPVL samples, quenched from the melt at a rate of 125°C min^{-1} and allowed to complete their crystallization for 3 min at 130°C (T_L), as a function of the maximum melt temperature, T_H, in the preceding heating cycle (indicated on each curve); 5 min hold time in the melt at T_H; all heating rates are 20°C min^{-1}. The first heating curve (I) is also reported: except for the final temperature T_H it is identical for all samples. The endotherms at 225–235°C and those at ~210–215°C correspond to the melting transitions of the α- and γ-PPVL modifications, respectively



Scheme 2

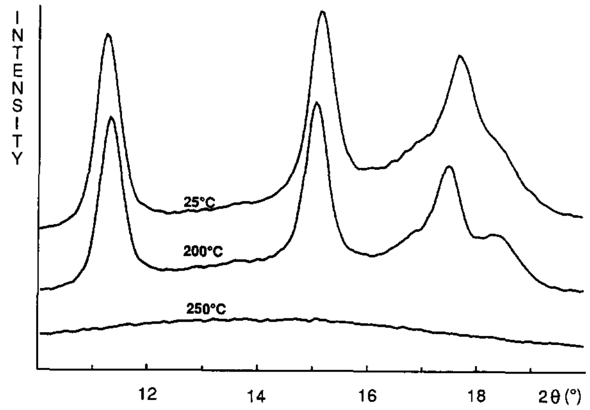


Figure 2 X-ray diffraction patterns of native PPVL recorded at 25, 200 and 250°C

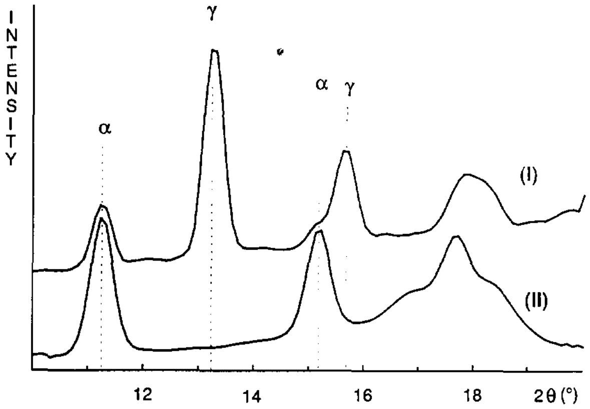


Figure 3 X-ray diffraction patterns of PPVL samples that have been treated in the differential scanning calorimeter as follows: (I) sample conditioned 3 min at 130°C, kept at 247°C for 5 min, cooled to 130°C and then allowed to complete its crystallization at that temperature, and (II) sample treated in an identical way to the sample in trace (I), but subsequently, however, kept at 225°C for 2 min, and then cooled again to 130°C. Heating and cooling rates are 20 and 125°C min^{-1}, respectively, in all cases

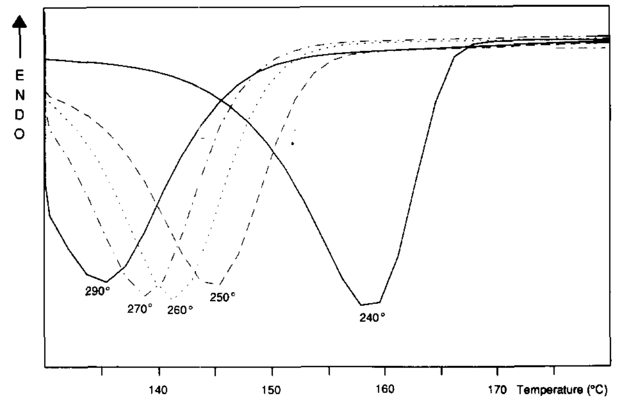


Figure 4 Crystallization behaviour (T_H–T_{L1} segment, see *Scheme 2*) of different PPVL samples, cooled at ~125°C min^{-1}, as a function of the melt temperature T_H (indicated on each curve). The samples are the same ones that have been previously discussed with respect to *Figure 1*

does not decrease significantly (i.e. <1°C) on increasing T_H from 240 to 290°C in the previous heating cycle. This is consistent with previous reports[6] showing very limited thermal degradation of PPVL in the absence of oxygen, for hold times of the order of a few minutes in the temperature range of interest.

Figure 4 shows the crystallization curves (see *Scheme 2*, segment T_H–T_{L1}) of the same samples, which were previously discussed with reference to *Figure 1*. We see that the crystallization temperatures vary appreciably with T_H. Specifically, the higher T_H the lower, apparently, is the crystallization temperature at the same cooling rate. Although the crystallization temperature difference between samples heated to 270 and 250°C is only ~5°C, with the data discussed above we cannot exclude that this difference, which could in principle also be due to thermal degradation, rather than T_H, determines the γ/α ratio. Indeed, with crystallization temperatures >180°C the γ-modification is virtually absent, no matter what the other conditions are[4,5]. Additional experiments show, however, that if the crystallization is carried out at a fixed temperature of e.g. 160°C, clearly different γ/α ratios are obtained as a function of T_H, with the result being confirmed both by thermal analysis (*Figure 5*) and X-ray diffraction (*Figure 6*). Inspection of *Figure 4* shows that with the cooling rate of 125°C min^{-1} used in the present experiments no significant crystallization occurs upon cooling down to temperatures below 160°C, which is therefore the actual crystallization temperature. It should be noted that the low crystallization temperatures reported in some previous papers (e.g. ~100°C, with cooling rates of 80°C min^{-1})[9,21] do not appear to be attainable with the apparatus used in those particular studies, and crystallization is likely to have occurred at considerably higher temperatures. In our case, with cooling rates of 80°C min^{-1} in the DSC-7 calorimeter, crystallization normally occurs in the 140–170°C range, depending, essentially, on the previous thermal history of the sample.

The evidence discussed so far suggests that while the crystallization temperature has some effect on the relative amounts of the two polymorphs which are obtained, as long as the crystallization temperature is between 140 and 160°C, the influence is relatively minor. The observed behaviour can be rationalized assuming that for crystallization in the reported temperature range, the melt temperature T_H, to which the samples have been exposed prior to crystallization, has a major influence:

(i) up to ~240°C, i.e. 5–10°C above the phenomenological melting point, a large number of α-crystals survive for at least 5 min in the melt and cause the specimen to crystallize quickly, at comparatively high temperatures and consequently, to display a somewhat higher melting point than samples brought to higher melt temperatures;

(ii) in the range between 250 and 280°C, some different 'nuclei' become active, causing γ-crystallization to occur; at the lower temperatures (~250°C) their influence is prevailing, but decreases as the melt temperature T_H is increased until:

(iii) for crystallization from temperatures T_H above 290°C, which are 20°C higher than the proposed equilibrium melting point of PPVL (269°C), where large nuclei cannot survive, only the α-modification is obtained.

The time for which the sample is kept at a specified melt temperature also appears to influence the subsequent crystallization behaviour. *Figure 7* shows the last heating stage of cycles identical to those previously discussed with reference to *Figure 1* and *Scheme 2* (full lines), with the only difference being that in the present case the specimens have been kept in the melt at 247°C (T_H) for different times t_H, namely 0.5, 4 and 20 min, before quenching them at a rate of 125°C min^{-1} to 130°C (T_{L1}).

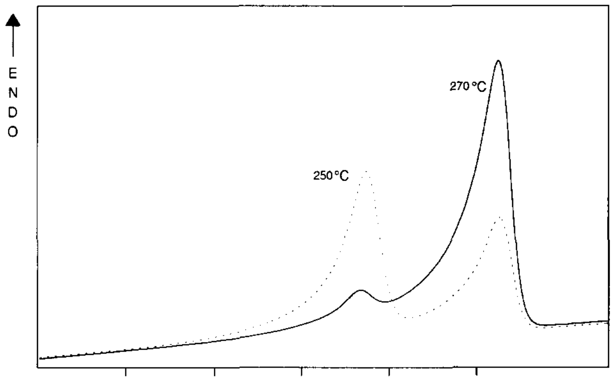


Figure 5 Melting behaviour of two different PPVL samples, quenched from the melt at 125°C min^{-1} and crystallized for 3 min at 160°C, for the two melt temperatures T_H (i.e. 250 and 270°C) indicated on each curve

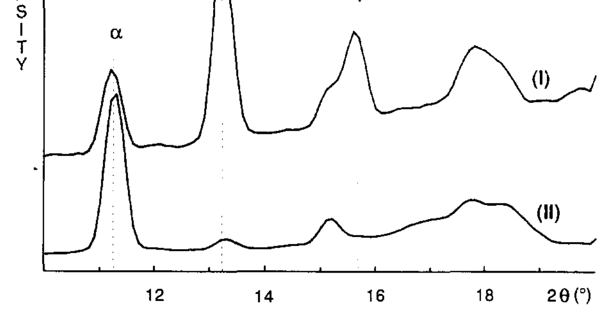


Figure 6 X-ray diffraction patterns of two different PPVL samples, quenched from the melt at 125°C min^{-1} and crystallized for 3 min at 160°C. Traces (I) and (II) refer to the samples with T_H values of 250 and 270°C, respectively

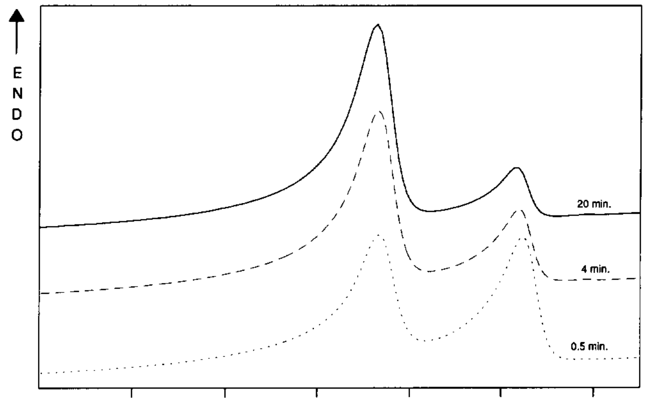


Figure 7 Melting behaviour of different PPVL samples, treated according to *Scheme 2*, and differing only with respect to the hold time t_H (0.5, 4, and 20 min) at the melt temperature T_H, which in all cases is 247°C. With $t_H = 0.5$ min the ratio γ/α is ~ 1, while the γ-phase prevails with longer hold times at T_H. The heating and cooling rates were 20 and 125°C min^{-1}, respectively, while the hold time t_L to complete crystallization at 130°C was 3 min

The α/γ ratios vary from ~ 1.0 for the sample kept at 247°C for half a minute, to ~ 0.15–0.10 for specimens held for longer times in the melt at that temperature. It is noteworthy that the crystallization temperatures (i.e. both the onset and the minimum of the exotherm peak) remain constant within one degree, independently of the hold time in the melt and, therefore, again the crystallization temperature is not the determining factor. This experiment suggests that as long as a substantial amount of α-crystals remains in the melt at 247°C (i.e. 15–20°C above the observed melting point of this phase), crystallization from this melt temperature in the α-modification is substantial, and also under conditions and in temperature ranges favouring the γ-form. With a longer hold time t_H the α-form seeds are likely to diminish and the γ-modification tends to prevail. The α/γ ratio approaches an asymptotic value, which is close to 0.1 with hold times of ~ 30 min. These findings are of interest because they show that the structural entities causing γ-crystallization to occur, display a substantial stability in the melt that remains, at least in part, all the way up to the equilibrium melting point. It is also apparent that at least for melt temperatures T_H of the order of 250°C, which are optimal for subsequent γ-form nucleation, depolymerization effects can be disregarded. The qualitative features of the present analysis are largely confirmed by annealing experiments.

It should be pointed out that traces comparable to those shown in *Figure 1* are obtained if the same sample is treated in successive cycles with continuously increasing T_H values (see *Scheme 2*, dotted lines), e.g. with $T_H = 250$°C, $T_{H1} = 260$°C, $T_{H2} = 270$°C, etc. Minor differences, especially for the short hold times t_H at low T_H values, may be due to annealing effects. The result of first bringing a sample to a high temperature T_H, say 270°C, and in the second cycle to a T_{H1} of 247°C, is substantially different (see *Scheme 2* and *Figure 8*). In fact, the amount of 'recovery' of the original T_{H1} behaviour depends both upon T_H and on the hold time t_{H1}. This recovery is never complete, and the higher the T_H value the lower is the degree of recovery. This behaviour suggests an irreversible melting of pre-existing structure entities and/or some thermal degradation effects that partially prevent the re-formation of the γ-phase nucleating entities. However, these recycling experiments confirm that thermal degradation cannot be the principal cause of the investigated phenomena. While exposure to temperatures of 270°C or higher may lead to some significant chain-end initiated depolymerization[23–25], our data show that such treatment favours the more stable[13] α-modification. The key issue of this study is, however, the fact that for PPVL samples kept at intermediate melt temperatures (i.e. in the range 245–270°C), the nucleation of a different and somewhat less stable crystalline phase is made possible. This event seems unrelated to molecular-weight reduction, and is at variance with other interesting cases of polymorphic behaviour as, for example, γ-isotactic polypropylene, which can be obtained by crystallization of very-low-molecular-weight fractions[26–28].

The last experiment that will be discussed is the heating of PPVL samples to a melt temperature T_H (e.g. 280°C) that almost suppresses the γ-crystallization and, in the subsequent fast-cooling cycle, quenching the sample, prior to the standard crystallization procedure, to an intermediate melt temperature T_{H1} (see *Scheme 3*), from which, under favourable circumstances, γ-crystallization occurs (e.g. 247°C). Allowing the sample to stand at the intermediate temperature T_{H1} (above the phenomenological melting point) even for 6 h does not increase in any way the amount of γ-modification obtained, with respect to samples treated only at T_H. This result, compared to the recycling experiments, supports the idea that the entities favouring γ-crystallization are not equilibrium features of the melt, but more probably crystalline nuclei surviving the macroscopic melting of both the α- and γ-modifications.

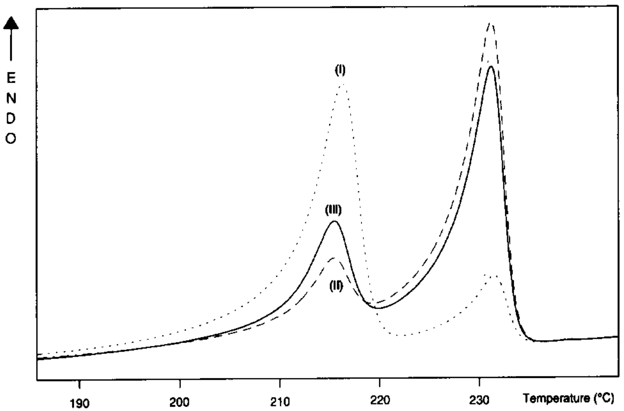
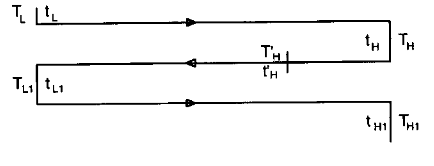


Figure 8 Successive heating scans for a PPVL sample treated according to *Scheme 2* (dotted line), with all of the heating and cooling rates being 20 and 125°C min^{-1}, respectively. Trace I is the heating cycle of a sample kept for 20 min (t_H) at 247°C (T_H), cooled to 127°C (T_{L1}) and allowed to crystallize for 3 min (t_{L1}). The heating cycle was completed at 270°C (T_{H1}) with a hold time t_{H1} of 3 s. After cooling the sample to 127°C (T_{L2}) and allowing it to crystallize for 3 s (t_{L2}), trace II was recorded. This trace was completed at 247°C (T_{H2}) with a hold time t_{H2} of 30 s. The sample was allowed to crystallize in the usual fashion at 127°C (T_{L3}) and the last heating cycle (trace III) was then carried out



Scheme 3

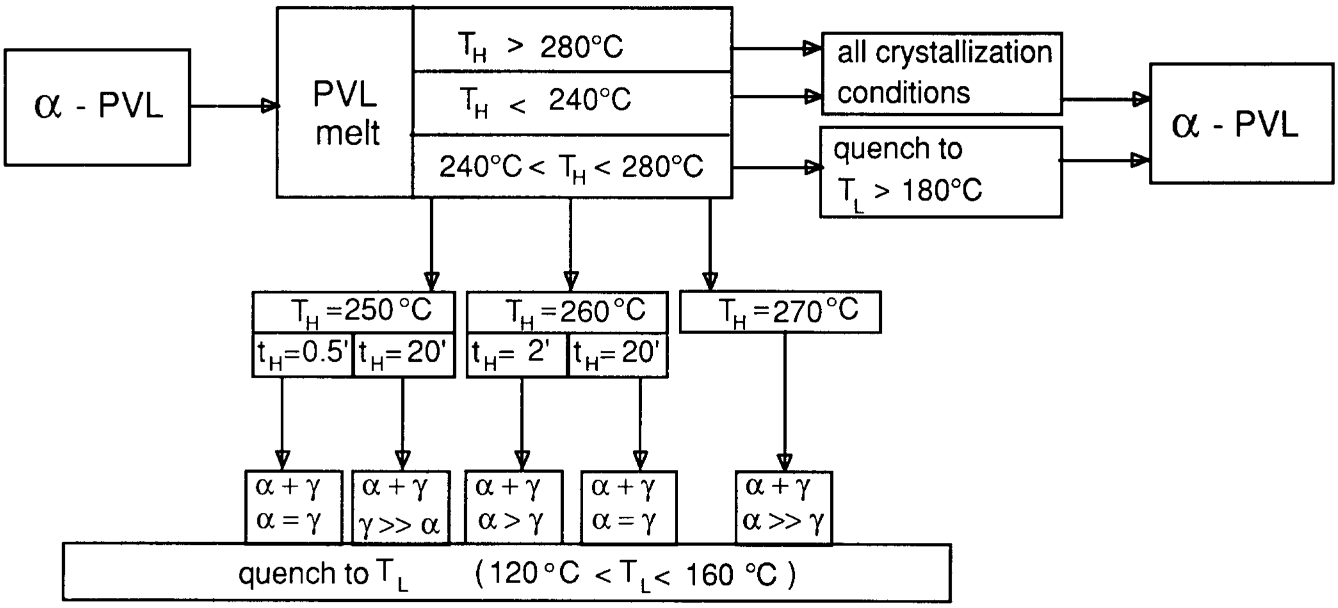


Figure 9 A summary of the polymorphic melt-crystallization behaviour of polypivalolactone. Samples of different origin display similar behavioural trends, although quantitative differences in the proportions of the two phases can occur. T_H represents the maximum temperature to which a sample has been exposed in the melt and t_H is the time spent at T_H, while T_L represents the temperature to which samples were quenched in the calorimeter and allowed to crystallize

CONCLUSIONS

The behaviour that we have found is remarkably similar to the one schematically reported[17] by Turner-Jones *et al.* for the melt crystallization of isotactic polypropylene (iPP) for a specific batch of polymer, but never reproduced nor clarified. In that study, heating of the iPP sample to 10–30°C above the melting point, and quenching it to the appropriate temperature, greatly enhanced the crystallization of a different polymorph (β-iPP), when compared to the normally crystallizing α-phase. Exposure to higher melt temperatures resulted again, according to these authors, in exclusive crystallization of the normal and more stable α-iPP. It is noteworthy that both in the case of iPP and PPVL the two different modifications are characterized by the same conformation, but substantially different packings. Similar, although less detailed, indications can also be found with respect to syndiotactic polystyrene[20], while the maximum solution temperature in the case of isotactic poly(1-butene)[18] and poly(4-methyl-1-pentene)[19] causes the crystallization of these polymers to occur with different polymorphs, characterized in the last two instances by (slightly) different conformations. These, according to Chau *et al.*[18] may relate to different conformations prevailing in solution at different temperatures.

A summary of the essential features of the polymorphic melt crystallization behaviour of PPVL is given in *Figure 9*. Different explanations can be suggested with the presently available experimental data. A first possibility is the presence of heterogeneous nuclei in all samples, favouring the crystallization of the γ-modification; this suggestion seems unlikely because the hypothetical 'heterogeneous nuclei' lose their nucleating ability at a temperature which is very close to the suggested equilibrium melting point of PPVL and regain, at least to some extent, their activity only after the polymer has been recrystallized. On the other hand, classical work by Binsbergen and coworkers[29,30] on heterogeneous nucleation in isotactic polypropylene established that the melt temperature from which samples were cooled did not affect the number of nuclei nor the kinetics in a range which was 100°C above the melting point of the polymer. Furthermore, PPVL is known to contain very low concentrations of foreign heterogeneous entities: with this polymer it is common to grow spherulites which are millimetres in diameter at temperatures of 190–215°C[1,2,4,5]. The second hypothesis, which appears to be more probable given the present evidence, is that although the native polymer is essentially all in the α-form, it may also contain γ-phase 'nuclei'. As long as these entities survive, if the number of residual α-crystals remaining in the largely molten sample is sufficiently reduced, and if appropriate crystallization conditions are used, γ crystallization can occur. These nuclei melt close to the equilibrium melting point of PPVL and can reform in limited number upon recrystallization. Appropriate annealing conditions can maximize their effectiveness. What remains unexplained is why the nuclei of a lower-melting modification should survive well above (i.e. more than 40°C) the melting point of the corresponding phase and ~30°C above the phenomenological melting point of the higher melting α-modification, which has been shown to be more stable[13] as far as the packing energy is concerned. If, in fact, α-nuclei similarly survive in comparable or larger numbers at a given temperature it is unclear why they should be substantially less effective in nucleating new crystals. Optical micrograph observations from previous work (see, e.g. Figure 2 in ref. 1 and Figures 25 and 26 in ref. 2) suggest that *the main cause determining the prevalence of either the α- or γ-modification is the number of active nuclei*, as can be estimated from the number of corresponding spherulites, rather than the relative crystallization rates. At high crystallization temperatures (i.e. ~180°C, or with slow cooling rates) under conditions that cause the α-modification to dominate, α-spherulites are frequent and large, while γ-spherulites are small and rare. In this situation the boundaries of the γ- with the α-spherulites are highly convex suggesting a significantly greater growth rate for the α-modification. If on the contrary, the two phases coexist in similar proportions, the number of spherulites appear to be comparable, whereas if the γ-phase predominates it is the number, rather than the size, of the spherulites that is responsible for the situation. Interestingly, in these conditions the shape of the α–γ spherulite boundaries also indicates that the growth rate for α-PPVL prevails. The present morphological comments are based on preliminary work and are therefore qualitative. More systematic and quantitative information would be helpful to establish the above conclusions more firmly.

A basic open question concerns the nature of the γ-phase nucleating entities. In this respect we can state that *the γ-phase nucleating entities are not likely to be large γ-crystals surviving in the melt because of their size.* The basis for this conclusion is that samples able to crystallize profusely in the γ-phase, i.e. exposed to melt temperatures at which γ 'seeds' appear to be stable and dominant, when crystallized at temperatures greater than 180°C afford basically the pure α-modification. A substantially smaller γ-phase crystallization rate, when compared to that of the α-phase, seems unlikely considering the evidence that has just been discussed. A more likely explanation for this behaviour is that γ seeds are too small to be effective at high temperatures and the small number of truly heterogeneous nuclei present are indeed the only ones able to initiate crystallization under those circumstances. At lower temperatures (170–120°C) the γ-like entities acquire the ability to nucleate, while at still lower temperatures α crystallization prevails again[3,16] as nucleation becomes more truly homogeneous, and is probably caused by density fluctuations rather than by γ-like structural organization surviving the phenomenological melting point. The entities that we have referred to so far as *γ-phase seeds could well be substantially more disordered and relate only in a rather distant fashion to the crystalline γ-phase*: the packing involved is likely to be a rotationally disordered hexagonal arrangement, typical of thermotropic mesophases. In this respect we note (see Figure 4 of ref. 13) that γ-PPVL approaches a hexagonal packing more closely than the α-modification, just as β-iPP is closer to hexagonal than the α-form, or for that matter, γ-iPP. *The key feature determining the relative stability with respect to α-PPVL crystals of the γ-PPVL seeds could well be of entropic nature.* However, these structural entities should involve only traces of material since a macroscopic high-temperature mesomorphic phase is incompatible with the diffraction patterns we observed at 250°C (see *Figure* 2). Metastable bundles of chains of the kind proposed, for example, by Allegra[31], could be a viable tentative model for such structural entities.

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