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Development of thermal stability of polymer crystals during isothermal crystallisation

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Abstract: In classic theories of polymer crystallisation, it is assumed that only the nuclei are in thermodynamic equilibrium with the melt. In Strobl's model of polymer crystallisation, a multi-step process is discussed. At the first intermediate states, the growing lamellar crystallites are assumed to be in equilibrium with the melt. After a stabilisation step, the lamella gains final stability. We have studied the stability of growing polymer lamellae by applying short temperature pulses. Changes in morphology were detected by simultaneous shear modulus measurements. The highest temperature reached during such temperature pulses was always below the final melting temperature. For poly(ε-caprolactone) (PCL) at 331 K it was found that temperature pulses of 4 K height and 300 s duration every 1 800 s prevented crystallisation totally. Lower pulses only slow down the crystallisation process. For syndiotactic polypropylene at 403 K, pulses of 14 K every 7 200 s were necessary to prevent crystallization. For PCL the kinetics of the crystallisation and stabilisation processes has been determined. A temperature pulse of 4 K height after 10 000 s isothermal crystallisation at 331 K totally destroys the already formed crystalline structures although the degree of crystallisation at this time is already 17%. With ongoing annealing time, the crystalline structure becomes more stable and the impact of the pulses decreases. After main crystallisation, when the crystallinity is basically constant, the amount of stable lamellae continuously increases. This indicates the occurrence of a significant stabilisation step after formation of the lamellae in PCL.

Introduction

Many engineering polymeric materials are used in the semicrystalline state. Despite this fact, some very basic questions regarding polymer crystallisation are still open. It is still a matter of debate whether or not the growth of a polymer crystal is a one-step or a multiple-step process. In the last ten years, there was increasing evidence that traditional theories of polymer crystallisation [1-4] do not describe the process correctly. New theories and models came up. Especially the experimental evidence of structural development at larger length scales at very early times of the crystallisation process [5-8] enforced the efforts to develop new theories. Most of these new theories treat the structural development only during the very early stages to understand the first step of an assumed multi-step process. But it is not yet clear if the event of polymer crystallisation starts by spontaneous spinodal decomposition, discussed by Olmsted et al. [9], or nucleation followed by growth as recently discussed by Muthukumar et al. [10,11] and Meyer et al. [12,13]. In 2000, a model for polymer crystallisation was introduced by Strobl [14]. It covers not only the initiating step, but the whole crystallisation process with a few specific steps, where these steps are considered to be universal. The model is not only an extension of existing models but considers quite different mechanisms. Two points should be mentioned here. (i) A metastable pre-ordered structure in the super-cooled melt is assumed. This structure should be in thermodynamic equilibrium with the surrounding melt. (ii) The crystalline lamella undergoes a stabilisation process without lamella thickening resulting in the final melting temperature. For most of the polymers, the final melting temperature is at least 10 K higher than crystallisation temperature. In Fig. 1, Strobl's model for polymer crystallisation is schematically shown for one growing lamella. Starting with a pre-ordered mesomorphic layer structure in the super cooled melt (right part of Fig. 1) the structure is transformed with time by a spontaneous thickening process into a granular crystal layer first.

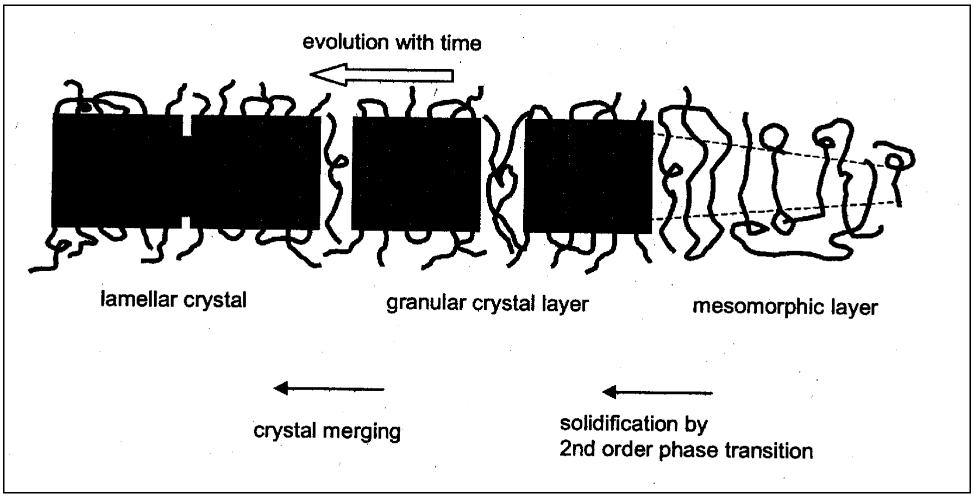

Fig. 1. Strobl's model for polymer crystallisation (from ref. [14])

The thickness of the just formed granules, and the thickness of the granular crystal layer, respectively, should be a function of the crystallisation temperature and equal to the thickness of the final crystal lamella. It is considered that no further lamella thickening happens during the following steps.

According to Strobl's view, the next step of the crystallisation process should be a stabilisation of the native granular crystalline structure. This stabilisation is considered as a merging of the single granules (also called blocks) to regular crystal lamellae. During this stabilisation step, the non-crystalline material between the granular crystallites becomes ordered and the intra-lamellar granular structure disappears. Consequently, the intra-lamellar surfaces disappear and the melting temperature increases with increasing intra-lamellar order.

Strobl was led to this model by experimental observations made in the last ten years by various research groups with new sensitive techniques like atomic force micro-scopy (AFM), *in situ* small-angle and wide-angle scattering. All the experimental results mentioned by Strobl are only indications of the existence of a metastable phase and a stabilisation process.

In this paper we address the question of a possible stabilisation process of the crystalline lamella with time. We show a way to verify the existence of a stabilisation process during isothermal polymer crystallisation. It will not be a prove of Strobl's model in general, but we will show if one has to consider a stabilisation process in models of polymer crystallisation or not.

Idea of the experiments

The stabilisation of a single lamella yields an increase of the melting temperature with time. The reason for such a stabilisation may be manifold. If lamella thickening occurs as in the case of polyethylene, the melting temperature increases as described by the Gibbs-Thomson equation. But also processes like internal reorganisation, resulting in a decreased internal surface as discussed by Strobl (block merging), yield a similar increase of the melting temperature. From the melting temperature dependence, one cannot distinguish between lamella thickening and internal lamella stabilisation. For some polymers it is known that they do not show lamella thickening during isothermal crystallisation. If these polymers also show a slight increase in melting temperature during isothermal crystallisation, a stabilisation process different from lamella thickening would be present.

According to Hoffmann and Lauritzen, the melting temperature of the crystals is fixed from the very beginning of the crystallisation process by the lamella thickness which is defined by the super-cooling. This is based on the assumption that a crystal lamella with its final structure grows into the melt. Just behind the growth front, the final crystal lamella is considered. If a polymer chain is once created in the crystal, it can be removed only by heating above the final melting temperature. In the Sadler-Gilmer theory [3,4], an extension of the Hoffmann-Lauritzen theory, a possible attachment and detachment of chain segments has been introduced only directly at the growth front of the lamella. No local equilibrium between the crystal behind the growth front and the melt is considered. Strobl, in contrast, assumes a stabilisation of the lamella behind the growth front. During this stabilisation, the total internal surface decreases from that of the granular structure (including intra-lamellar surfaces) to that of the regular lamellar structure. With the decreasing surface, the surface free energy becomes lower. According to the Gibbs-Thompson relation, this yields a continuously increasing melting temperature until the final value is reached, not assuming any lamella thickening. In Fig. 2, the development of the melting temperature of a single lamella is shown schematically for both cases.

According to Hoffmann and Lauritzen, crystallisation of the particular lamella starts after an induction time due to nucleation. The induction time depends on the crystallisation conditions. Just after formation of the lamella, its melting temperature equals to the final melting temperature (blue line). The arrow schematically shows the development of the melting temperature regarding to Strobl's model, which includes an ongoing stabilisation process and consequently an increasing melting temperature with increasing degree of stabilisation. The induction time before crystallisation is again defined by the crystallisation conditions (mainly nucleation density and super-cooling). After a certain time the lamella gains its final stability, and consequently the melting temperature does not further increase and equals the final melting temperature. According to Fig. 2, as a first approximation the stabilisation process is considered to be linearly increasing with time for isothermal crystallisation. In reality this is not necessarily the case, but can be proved by the method described next.

The measurement of the melting temperature of a single lamella is a difficult task. It needs a spatially resolved measurement on a nanometer scale which is actually only possible by means of AFM and not available for bulk samples. By electron microscopy (TEM) [15] or standard thermal analysis techniques like differential scanning calorimetry (DSC) and shear spectroscopy (DMA), it is possible to test the stability of all lamellae grown until a certain time by applying a certain increase of temperature and to study the resulting changes in morphology. Because the imaging techniques are time consuming due to sample preparation, it may be helpful first to perform DSC and DMA measurements to obtain general information in a wide range of experimental conditions.

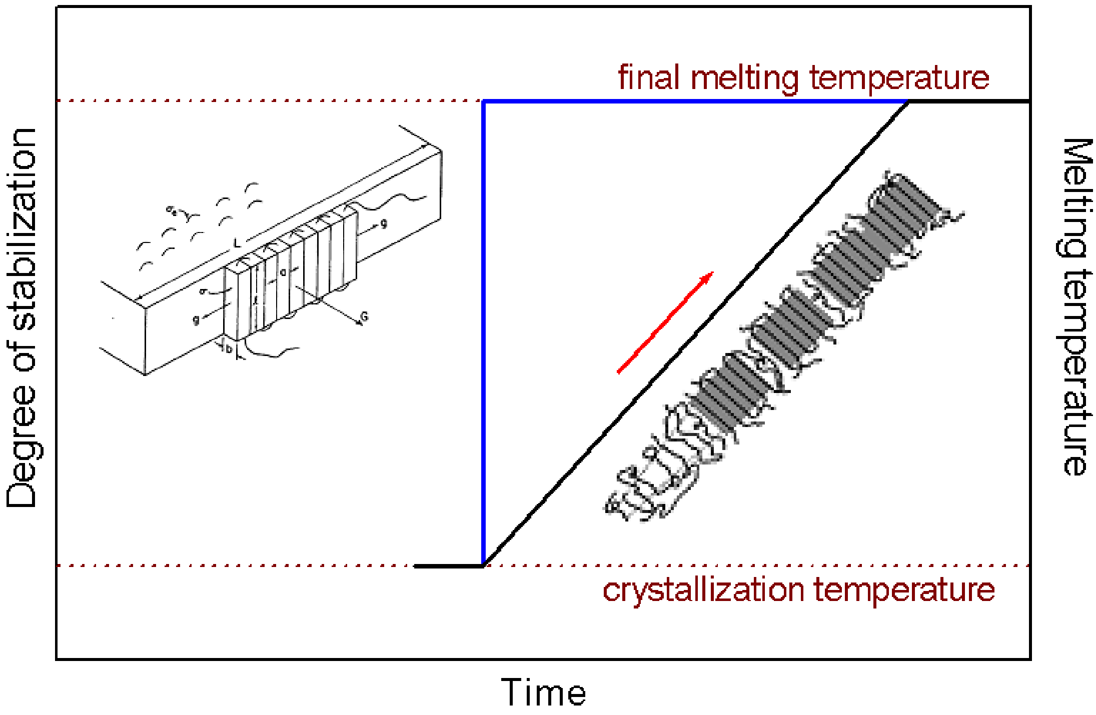

Fig. 2. Comparison of different models for polymer crystallisation with regard to the development of stability and melting temperature of a single crystallite during isothermal crystallisation

A first step to determine the time dependence of the melting temperature during isothermal crystallisation is to check the necessary temperature increase to destroy the just formed crystalline structure. This could be done by a short heating pulse after a certain time. If the crystal has already reached the final stability and no stabilisation takes place, the maximum temperature of the pulse has to be necessarily equal or above the final melting temperature of the stable crystals (see Fig. 3a). On the other hand, if a partly stabilised structure is formed after a certain annealing time then - compared to the final melting temperature - a lower temperature pulse would be sufficient to destroy the growing lamella. This situation is schematically shown in Fig. 3b. The maximum of the temperature pulse is higher than the actual melting temperature of the crystal. Consequently, the lamella melts and crystallisation has to start from the beginning. Such a pulse with a maximum temperature below the final melting temperature would not influence the stable crystals. Of course, the annealing time before applying the temperature pulse and the maximum temperature of the pulse are not independent parameters as will be discussed below.

Up to now, only one particular lamella has been considered. If the same approach is extended to a number of successively growing lamella, a distribution of induction times would be given before the start of crystallisation. This is shown schematically in Fig. 4a, were the formation and the stabilisation of various crystallites is taken into account.

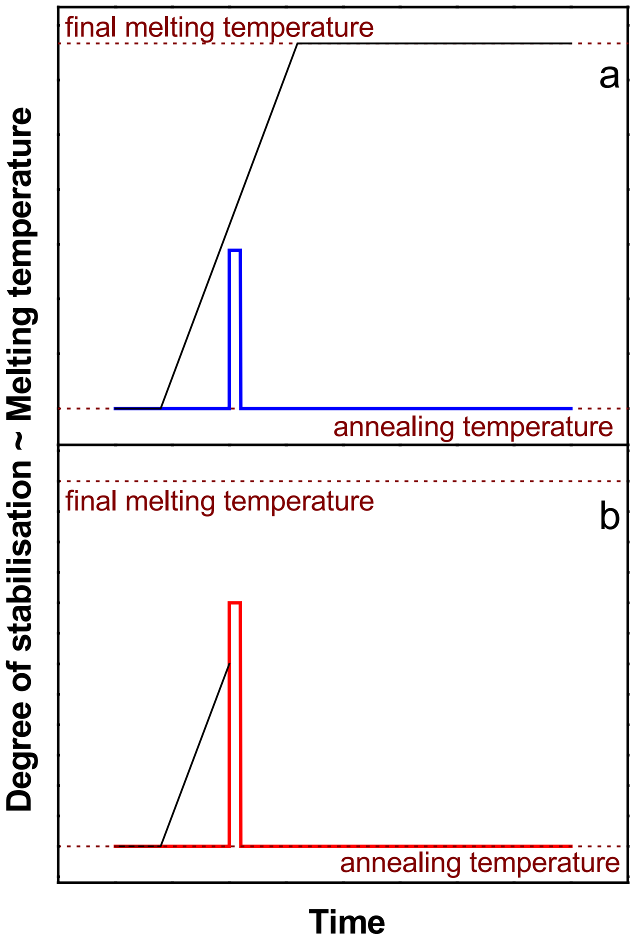

Fig. 3. Influence of temperature pulses of different height on the crystallisation of a single crystallite

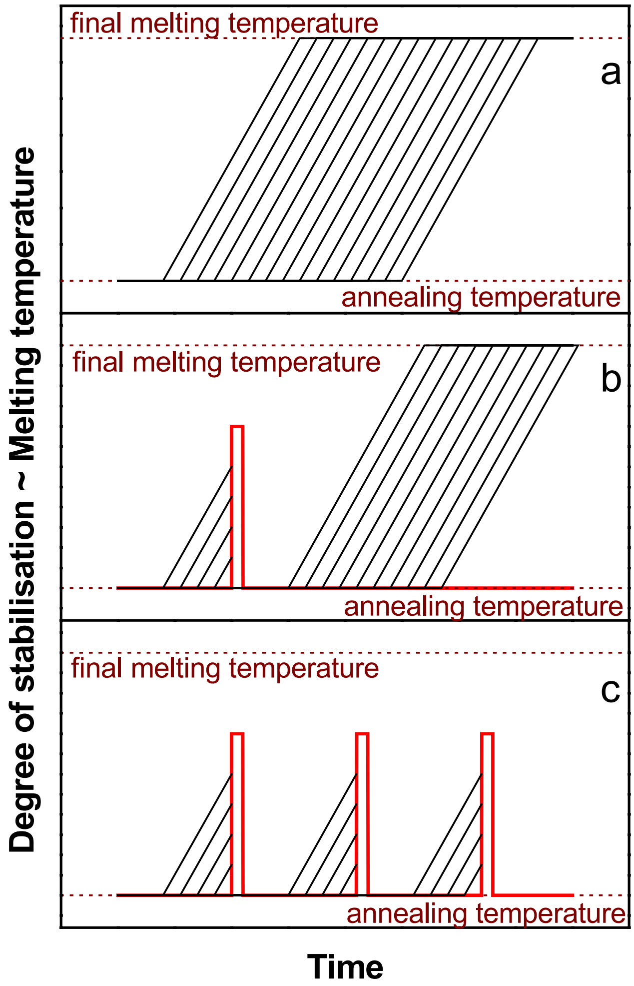

Fig. 4. Influence of temperature pulses on crystallisation

If a temperature pulse with a certain maximum temperature is applied after a certain crystallisation time, all the semi-stable crystals formed previously would be destroyed as shown in Fig. 4b. In this case the crystallisation has to start again. If such a temperature pulse is repeated, the crystallisation can be prevented completely as shown in Fig. 4c. Assuming no stabilisation, one would not be able to prevent crystallisation by temperature pulses below the final melting temperature of the lamella applied at significantly longer times as the duration of the induction period. Therefore, such experiments will prove the appearance of any stabilisation process during isothermal crystallisation.

Experimental part

To carry out the experiments described above, some sensitive methods have to be employed to follow the time and temperature dependent changes of the crystalline structure. Because the mechanical properties of a polymer strongly depend on crystallinity, Dynamic Mechanical Analysis (DMA) can be used suitably. The device used for this study was the Advanced Rheometric Expansion System (ARES) from Rheometric Scientific with a parallel plate geometry. The diameter of the plates and samples was 25 mm, and their thickness was between 0.5 and 1 mm. The measured quantity is the shear stress (σ) in response to the applied shear strain (γ). From shear stress and shear strain one can calculate the complex mechanical modulus G^*. We discuss the time and temperature dependence of the real part of the shear modulus G' because it changes for several orders of magnitude during crystallisation of a polymer.

As described above, it is necessary to perform these studies with samples showing no lamella thickening. Poly(ε-caprolactone) (PCL) and syndiotactic polypropylene (sPP) are chosen because X-ray studies showed constant lamella thickness during isothermal crystallisation [16,17]. The PCL sample with molecular weight M_w = 55 700 g/mol was obtained from Sigma-Aldrich and the sPP sample (M_w = 150 000 g/mol) from Atofina.

For PCL it is possible to follow the isothermal crystallisation by DMA experiments and to estimate the degree of crystallinity from changes in the storage modulus [18]. The applied low shear strain (γ_0 = 0.1% - 10%) was proven not to influence the crystallisation kinetics [19].

Results

First, the existence of a stabilisation process was confirmed for PCL and sPP. This was done by applying temperature pulses in series during isothermal crystallisation as described above (see Fig. 4c). The PCL sample was cooled with 1 K/min from the melt at 345 K to the annealing temperature of 331 K. According to Fig. 4c, temperature pulses have been applied with different pulse heights between 0.5 K and 4 K every 1 800 s. The annealing time at the maximum temperature was 5 min. This seems to be long enough to reach steady state for sample temperature. The final melting temperature of PCL for this crystallisation conditions is 337 K. With the highest temperature pulses of 4 K, the maximum temperature reached was 335 K which is still below the final melting temperature.

The measured storage modules (upper part) and the temperature profiles (lower part) are shown as functions of time in Fig. 5. Let's first focus on the red curve in the upper part, which represents temperature pulses with 0.5 K height. After about 7 500 s (5 000 s at the 331 K) the storage modulus starts to increase. This is the point where crystallisation starts and first crystals are formed. If one compares the development of the storage modules for temperature pulse heights of 0.5 K (red curve), 1 K (green curve) and 2 K (blue curve), no differences in the overall behaviour compared to isothermal conditions (black curve) are visible. Consequently, the temperature pulses have no or only a minor influence on the crystallisation process. The decrease of the modulus during heating and the increase during cooling results from the temperature dependence of the storage modulus. This effect becomes, of course, larger with larger temperature pulses.

In contrast, pulses of 3 K height (light blue curve) slow down the crystallisation process strongly. The easiest explanation for this behaviour is that crystalline material melts during heating to the maximum temperature of the pulse. In this case, a slower increase of crystallinity and G' would be expected. On further increasing the height of the temperature pulses up to 4 K (magenta curve), no crystallisation takes place. With this temperature pulse series, where the maximum temperature of the pulses is almost 2 K below the final melting temperature, all crystalline material formed within 30 min is destroyed. The presented first 25 000 s of the experiment are representative of the whole measurement which takes longer than one day (*c.*

100 000 s). Crystallisation was prevented for the whole experiment when the highest temperature pulse (4 K) was employed every 1 800 s.

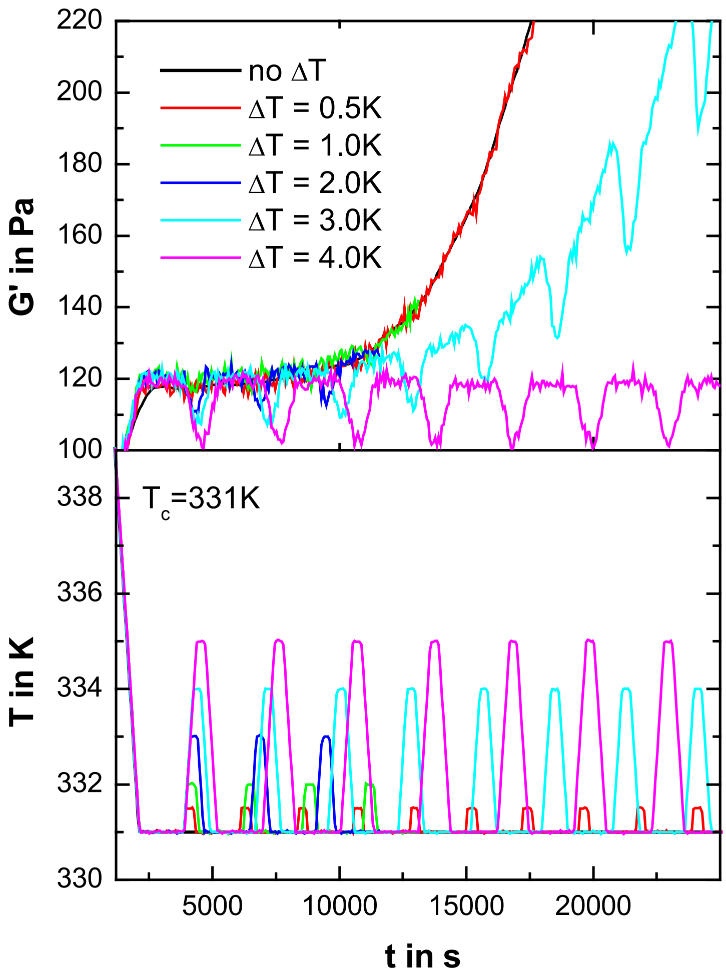

Fig. 5. Development of the storage modulus during crystallisation of PCL at 331 K as a function of time, for temperature pulse series of different heights

Fig. 6 shows similar experiments with sPP, where the sample was cooled from the melt at 423 K to the annealing temperature of 403 K. First, the development of the mechanical storage modulus during isothermal crystallisation without temperature pulses was measured (black curve). The slight increase of *G*' after about 30 000 s represents the beginning of the crystallisation process. Next, crystallisation experiments with temperature pulse series of different pulse heights above the annealing temperature of 403 K were performed. For pulses at every 7 200 s with heights of 5 K, 10 K and 12 K, only a small influence on the crystallisation process was found. However, a pulse height of 14 K prevented crystallisation totally. The maximum temperature of these pulses is 417 K and is about 3 K below the final melting temperature of sPP crystallised at 403 K.

Temperature pulses can be further used to study the kinetics of the stabilisation process. A temperature pulse of a certain maximum temperature applied after a short annealing time will destroy all the present crystals as long as they have not reached the necessary stabilisation to survive this pulse (Fig. 7a). If a longer annealing time is employed before applying the temperature pulse of the chosen maximum temperature, the first grown crystals are already stabilised and will not be melted by the temperature pulse. Only the youngest, less stable crystals will be destroyed by this pulse (Fig. 7b). When the annealing time is extended further, the ratio between unaffected and destroyed crystals becomes higher (see Fig. 7c and 7d). This allows the determination of a time dependent degree of stabilisation with respect to the chosen height of the temperature pulse.

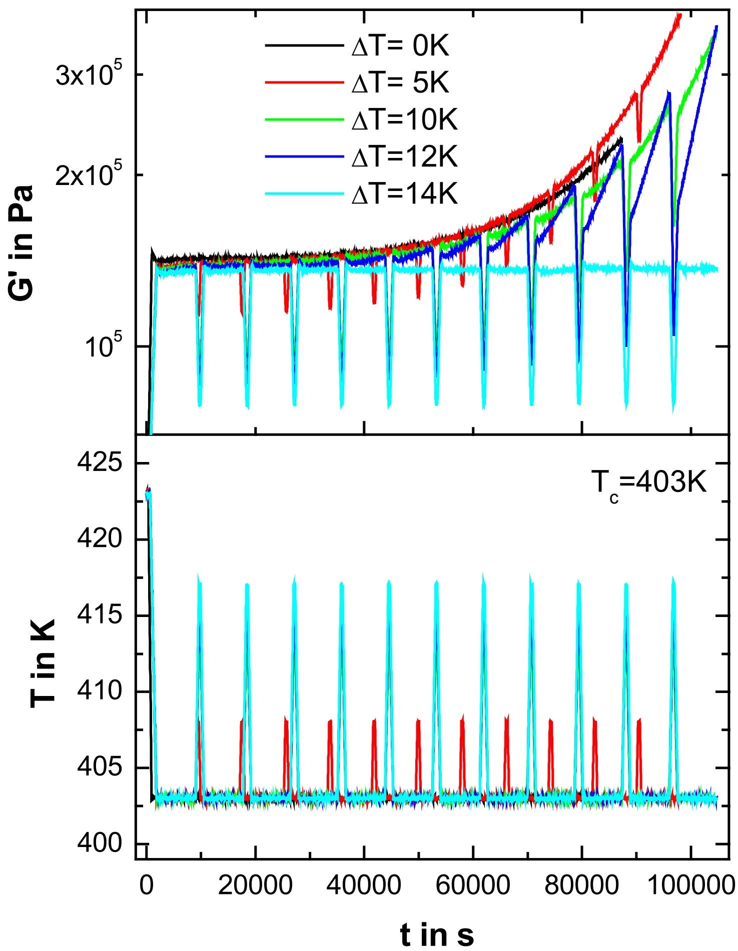

Fig. 6. Development of the storage modulus during crystallisation of sPP at 403 K as a function of time, for temperature pulse series of different heights

The influence of a single temperature pulse of 4 K height applied after different annealing times on the crystallisation process of PCL was checked as shown in Fig. 7. The development of the storage modulus for annealing times of 5 000 s, 10 000 s, 15 000 s, 25 000 s, 40 000 s and 80 000 s before applying the single temperature pulse is shown in Fig. 8. Let's first focus on the black curve, with an annealing time of 5 000 s at 331 K. After about 6 000 s (annealing time at 331 K is almost 4 000 s) the storage modulus begins to increase, which indicates that crystallisation takes place. About 1 000 s later, when crystallisation proceeds further, the temperature pulse was applied. During heating to 335 K, the storage modulus decreased to the value of the melt. After cooling back to the annealing temperature, the measured storage modulus gave the value of the storage modulus of the melt at 331 K. This indicates that the crystalline material was melted during the temperature pulse. With further annealing at 331 K, crystallisation reappears. The corresponding increase of the storage modulus is observed after about 12 500 s. This corresponds to a second annealing time at 331 K of 4 000 s. This annealing time equals the induction time after the first cooling from the melt. It seems that nothing remains from the crystals formed during the first annealing before the temperature pulse. The crystallisation process has to start with all its single steps from the very beginning. This indicates that temperature increase during the temperature pulse destroys all crystalline and ordered structures in the sample.

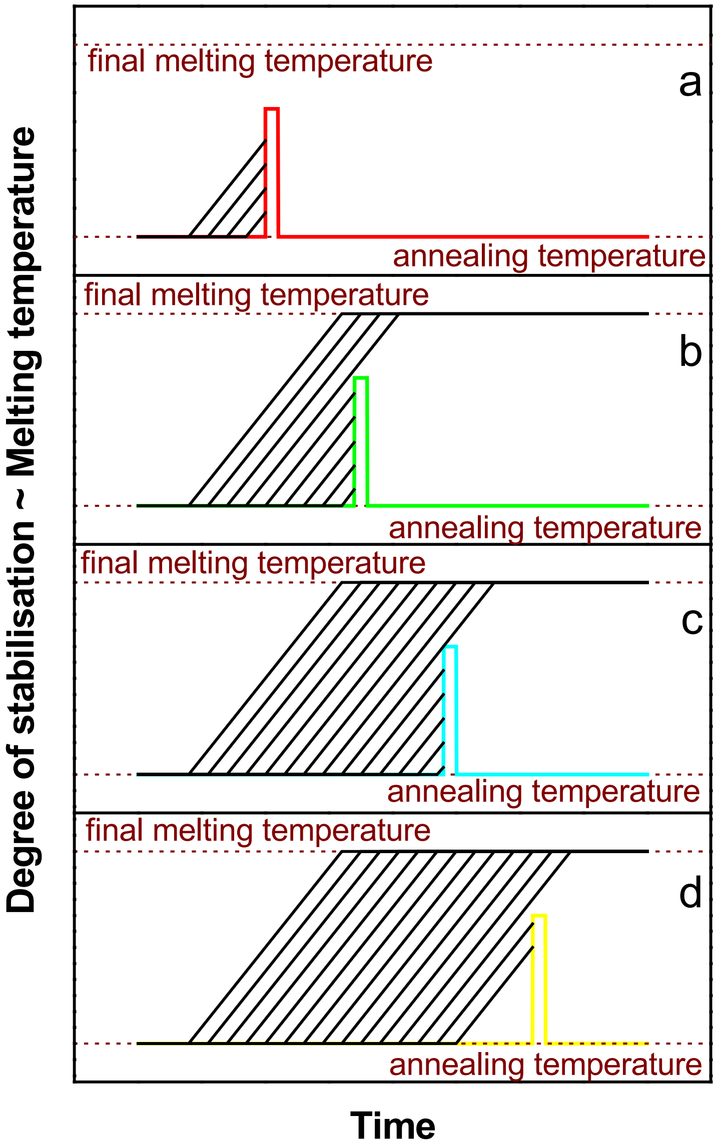

Fig. 7. Influence of temperature pulses after different annealing times on the crystallisation process

The situation changes after annealing for 10 000 s before the temperature pulse was applied (red curve). Again crystallisation begins after about 4 000 s annealing time and proceeds until the temperature pulse was applied. After the temperature pulse, the measured storage modulus again equals the value of the melt, but now crystallisation starts immediately after cooling to 331 K. No induction period was necessary. Considering the decrease of *G*’ to the value of the melt, it can be concluded that all crystalline material was melted during heating. But the fact that no induction time was necessary to resume crystallisation suggests that a small amount of ordered or crystalline structures remained.

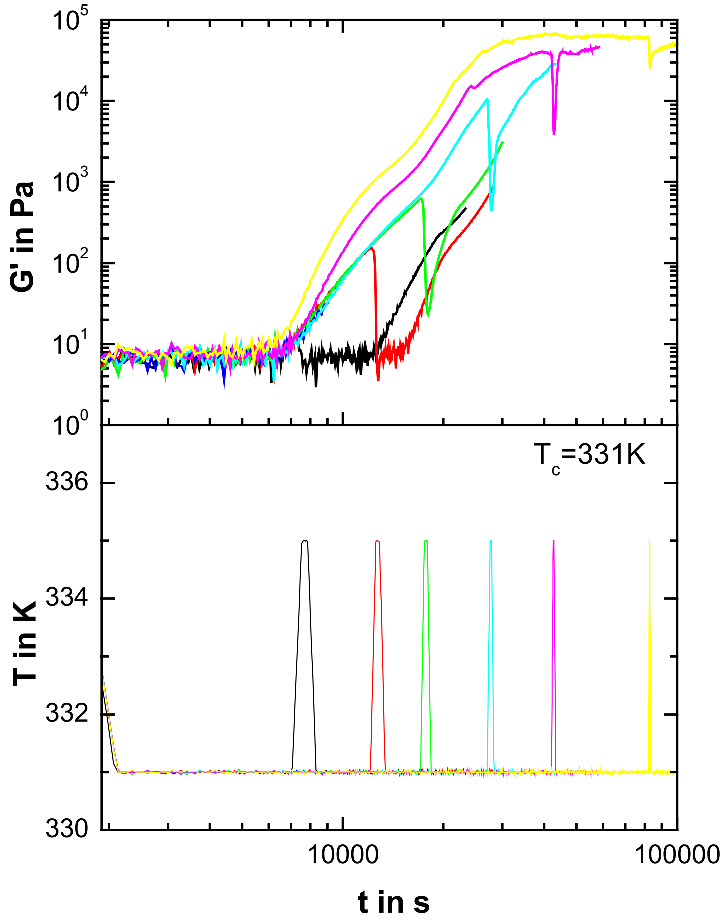

Fig. 8. Development of the storage modulus during crystallisation of PCL at 331 K as a function of time, for different annealing times before application of temperature pulses of 4 K height

Single temperature pulses after longer times of crystallisation do not destroy all crystalline material. One can observe a strong decrease of the storage modulus, but it does not reach the value of the melt as can be seen in Fig. 8 (green, light blue, magenta and yellow curves). This shows that a significant amount of crystalline material remains after the temperature pulse. A closer look to the steps in the storage modulus as a response to the temperature pulse reveals that the influence of the temperature pulses after longer annealing times becomes smaller and smaller. In other words, the influence of pulses on crystallization decreases with increasing annealing time which strongly supports the idea of stabilisation.

Discussion

Let's compare the effects of temperature pulse series on PCL and sPP with predictions of the different models of polymer crystallisation. For traditional models, where a stable lamella is assumed just behind the growth front, it would never be possible to melt the lamella by a temperature increase below the final melting point. But this melting was observed for PCL and sPP (see Fig. 5 and Fig. 6). For temperature pulse series as applied in our experiments, one would only expect a decrease of the total crystallisation rate in comparison to isothermal crystallisation. This is caused by the shorter total annealing time at the crystallisation temperature. Because of the small super-cooling and the resulting slow crystallisation kinetics, the annealing during the pulse at high temperatures would not contribute to the development of the crystalline structure.

If one assumes a stabilisation process of the lamella behind the actual growth front, one would expect the possibility to prevent crystallisation by a temperature pulse series (see Fig. 4c). For crystallisation of PCL at 331 K, it was shown (Fig. 5) that temperature pulses of 4 K every 1 800 s are sufficient to prevent crystallisation. For crystallisation of sPP at 403 K, it was shown (Fig. 6) that temperature pulses of 14 K were necessary every 7 200 s periodically to destroy the native crystalline lamella and consequently to prevent crystallisation. The highest temperatures during the pulses are below the final melting temperature (2 K for PCL and 3 K for sPP). These results strongly support the multi-step crystallisation theory, where a stabilisation process behind the growth front of the lamella is assumed.

In the light of Strobl's model, one would expect the formation of a granular lamellar structure during isothermal annealing at the crystallisation temperature. The melting temperature of this crystalline structure increases with ongoing block-merging. If one heats the sample during the pulses above the actual melting temperature of the granular lamellae, they will be destroyed. This process happens periodically by applying a series of temperature pulses.

The necessary height of the temperature pulses to prevent crystallisation depends obviously on the stability of the lamella and, therefore, on the annealing time at the crystallisation temperature. Further experiments have to be done to obtain information about the interplay between crystallisation temperature, annealing time between the pulses and necessary pulse height to prevent crystallisation. Also the influence of the annealing time at high temperature during the pulses has to be checked. All these interdependent parameters are assumed to be different for different polymers because of different crystallisation and stabilisation kinetics.

To get information about the kinetics of the stabilisation process for PCL, single temperature pulses after different annealing times at the crystallisation temperature were applied (Fig. 8). The influence of a single temperature pulse depends on the annealing time. Under the assumption of a stabilisation process, this was expected because of changes in the crystalline morphology.

To quantify the degree of stabilisation, the relative decrease of the storage modulus in response to the temperature pulse was estimated in the following way:

First, the storage modulus after isothermal annealing was measured (G'_{before}). This value depends on annealing time and crystallinity. Then the storage modulus immediately after applying the temperature pulse was measured (G'_{after}). Because of the melting processes during the temperature pulse, this modulus will be lower. The difference between G'_{before} and G'_{after} depends on the degree of stabilisation. The lower the measured difference, the higher the degree of stabilisation. Because of the large changes of the storage modulus with increasing crystallinity, it is not possible to compare the differences between G'_{before} and G'_{after} for different annealing times directly. But it is possible to normalise this difference to the maximum possible difference. This maximum possible difference is given by the difference between the measured modulus before the temperature pulse and the modulus of the melt (G'_{melt})

at the crystallisation temperature. This relative change of the storage modulus gives the fraction of unstable lamellae. The degree of stabilisation is than defined as:

$$\chi_{stabilisation} = 1 - \frac{G'_{before} - G'_{after}}{G'_{before} - G'_{melt}} \quad (1)$$

Because the storage modulus after the temperature pulse depends obviously on the height of the temperature pulse, one has to give this quantity with respect to the height of the temperature pulse or melting temperature of non-stable lamellae. The three different values of the storage modulus are marked in Fig. 9a for a temperature pulse of 4 K height after 15 000 s isothermal annealing of PCL at 331 K.

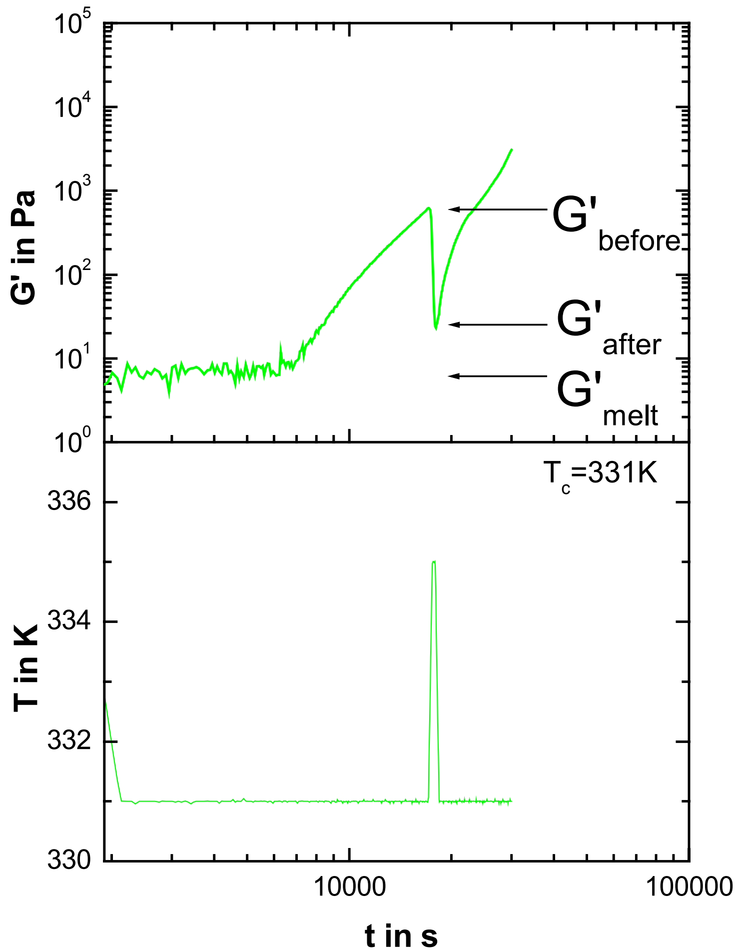

Fig. 9. Development of the storage modulus during crystallisation of PCL at 331 K as a function of time for an annealing time of 15 000 s before a temperature pulse of 4 K. From the marked values one can calculate the degree of stabilization

This calculation was done for different annealing times as shown in Fig. 8. The result is an increasing degree of stabilisation with increasing annealing time. The dependence of the degree of stabilisation on the annealing time is shown in Fig. 10 (red points). For annealing times of 5 000 s and 10 000 s, the measured storage modulus after the temperature pulse equals the modulus of the melt. All lamellae formed up to this time are molten during the temperature increase of 4 K. They are not stable with respect to a temperature pulse of 4 K height. Consequently, the degree of stabilisation is zero. No lamella survived the temperature pulse. After longer annealing times, the degree of stabilisation becomes higher. It can be suggested that more and more lamellae survive the temperature pulse, i.e., they are stable with respect to a temperature pulse of 4 K height.

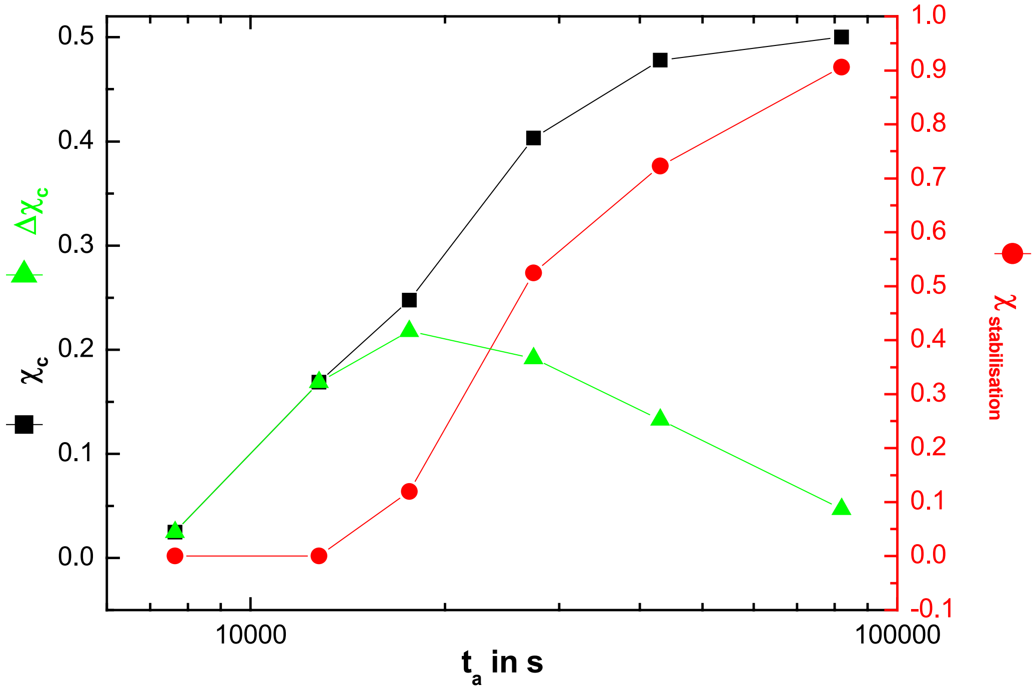

Fig. 10. Degree of stabilisation ($\chi_{stabilisation}$, ●), crystallinity (χ_C , ■) and decrease in crystallinity during the temperature pulse of 4 K ($\Delta\chi_c$, ▲) for PCL after different annealing times at 331 K

From the degree of stabilization it is impossible to estimate the amount of stable and unstable material. To obtain information about changes in crystallinity from the same measurement, the degree of crystallinity has to be estimated from the changes in the storage modulus. The relationship between storage modulus and crystallinity is very complex. A lot of sample properties which are not known for most of the polymers are needed to describe this relationship with theories taking into account combinations of amorphous and crystalline parts in the sample. So it is difficult to estimate changes in crystallinity quantitatively from shear modulus measurements. The estimation of crystallinity from the storage modulus was done in ref. [18] for PCL, where the relation between storage modulus and crystallinity was derived from simultaneous measurements of storage modulus and changes of the sample volume during isothermal crystallisation. By applying the same method to the data of Fig. 8, we can directly compare the annealing time dependence of the degree of stabilisation (red points in Fig. 10) with the annealing time dependence of crystallinity (black squares in Fig. 10).

Comparison of the degree of stabilisation and crystallinity gives two remarkable results. First, after an annealing time of 15 000 s, when it is still possible to destroy the whole crystalline structure with a single temperature pulse of 4 K, the degree of crystallisation is already 17%. This is about one third of the maximum crystallinity for PCL at these crystallisation conditions. Second, at longer annealing times between 40 000 s and 80 000 s, one finds only a small increase in crystallinity from 0.48 to 0.5. Only a fraction of new crystals are forming during this time. This period is often called ‘secondary crystallisation’. In contrast to this small increase in crystallinity, the degree of stabilisation increases in the same time interval from 0.73 to 0.91. After 40 000 s, still more then one quarter of the crystalline material (degree of stabilisation is 0.73) does not survive the temperature pulse, whereas after 80 000 s less than one tenth (degree of stabilisation is 0.91) of the crystalline material is destroyed by the temperature pulse. The different behaviour of crystallinity and degree of stabilisation in this time interval clearly indicates the existence of a stabilisation process. Crystallisation kinetics and the kinetics of the stabilisation process show different time dependences.

From the degree of stabilisation and crystallinity, one can also calculate the absolute decrease in crystallinity during the temperature pulse:

$$\Delta\chi_C = \chi_C(1-\chi_{stabilisation}) \quad (2)$$

The calculated values after different annealing times are shown as green triangles in Fig. 10. After short annealing times, if the whole crystalline material will be destroyed during the temperature pulse, this decrease in crystallinity is obviously identical with the crystallinity itself. After an annealing time of 15 000 s at 331 K, the decrease in crystallinity during the temperature pulse is 0.22. In other words, 22% of the sample is transferred (during the temperature pulse) from an ordered crystalline to a less ordered non-crystalline structure. This is about one quarter of the whole sample which suggests that not only nuclei but well developed crystals are also less stable with regard to a 4 K temperature increase.

For longer annealing times, the decrease in crystallinity becomes smaller. After an annealing time of 80 000 s, only 5% of the sample does not survive the temperature pulse. This is the consequence of the ongoing stabilisation with time.

If one wants to discuss the degree of stabilisation and its time dependence, it is always necessary to define it with respect to a certain pulse height or melting temperature of the unstable lamella. The time dependence of the degree of stabilisation and the kinetics of the isothermal stabilisation process were determined for PCL at 331 K by applying temperature pulses of 4 K height after different annealing times. The degree of stabilisation increases at the beginning of the crystallisation process slower than the degree of crystallinity. At longer annealing times, during secondary crystallisation, the situation is different. The degree of crystallinity is increasing very slowly whereas the degree of stabilisation increases fast.

Conclusion

An increasing melting temperature with time during isothermal crystallisation can be considered as the result of a stabilisation process. The stabilisation process was followed in time and magnitude by shear spectroscopic measurements (DMA), applying different temperature pulses to test the stability of certain structures. The reason for such a stabilisation could be lamella thickening or processes like internal reorganisation as discussed by Strobl [14]. To verify the existence of an intra-lamellar stabilisation, one has to exclude stabilisation due to lamella thickening. For PCL and sPP, no lamella thickening was observed during isothermal crystallisation [16,17]. For these two polymers, a stabilisation during crystallisation appears to support strongly the occurrence of an intra-lamellar stabilisation process different from lamella thickening.

For PCL it was shown that stabilisation is significantly slower than crystallisation. Consequently, both processes must be considered to be independent. This supports the idea that polymer crystallisation is a multi-step process. All our results can be explained by crystallisation theories including a stabilisation after growth behind the growth front, as in Strobl's model.

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