

Evidence for a mechanically active high temperature relaxation process in syndiotactic polypropylene

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Abstract

Frequency- and temperature-dependent dynamic mechanical tests on syndiotactic-polypropylene (s-PP) show the existence of a relaxation process at the high temperature or low frequency-side of the dynamic glass process. Its frequency is about 10^{-1} Hz at 100 °C and varies with temperature in an unusual manner, non-Arrhenius like, with an upward curvature with increasing temperature. The blocky substructure found for the crystalline lamellae of s-PP and the strain control of the deformation behavior, which needs more degrees of freedom than offered by stacks of internally stiff crystal lamellae, favors the assignment of the new process to intralamellar block slips. The assignment finds support in the observed retardation of the process accompanying a crystal thickening and the isotropy of the associated mechanical relaxation strength in an oriented sample. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years we have studied the yielding behavior of semi-crystalline polymers under uniaxial tensile forces by measuring true stress–true strain curves. Experiments were first carried out for a series of linear, branched and copolymerized polyethylenes with various crystallinities [1,2] and then also for syndiotactic polypropylene (s-PP) [3]. The results of the mechanical tests and accompanying wide angle X-ray scattering (WAXS) texture determinations demonstrated that the deformation behavior under tensile stress follows a general scheme. There exist always four critical points where the differential compliance, the recovery properties and the strain induced texture variations change simultaneously. We interpreted the associated alterations of the deformation mechanism as

1. the onset of single interlamellar and intralamellar slip processes (point *A*);
2. a turnover into a collective activity of slips (point *B*);
3. the beginning of fragmentation of the lamellar crystallites followed by the formation of fibrils (point *C*);
4. the beginning of chain disentangling (point *D*).

An important finding is that the strains at the critical points *A–C* are invariant. For polyethylene it was observed that the (Hencky-) strains at the critical points *A–C* were constantly at $\epsilon_H \approx 0.03, 0.1, \text{ and } 0.6$, independent of the crystallinity which varied between 80 and 10%, the temperature which was changed between ambient and a few degrees below the final melting, and the strain rate with values between 10^{-4} and 10^{-2} s^{-1} . In the case of s-PP we investigated one commercial sample under variation of the temperature and the strain rate and found again constant critical strains, now located at $\epsilon_H \approx 0.04, 0.12, \text{ and } 0.4$. In contrast to the invariant strains, the stresses at the critical points change greatly. They may decrease by more than one order of magnitude on lowering the crystallinity, heating samples up to the region of final melting or choosing a lower deformation rate. The findings first of all indicate that tensile deformations of semi-crystalline polymers like polyethylene and polypropylene are strain-controlled. The crystal texture in the sample reacts in a well-defined manner with the externally imposed strain. This simple strain controlled, which implies purely geometric, reaction is hard to understand if semi-crystalline polymers are viewed as being composed of stacks of laterally extended, internally rigid crystal lamellae. It becomes conceivable, however, if one recognizes that the lamellar crystallites possess an internal blocky substructure. This property is well known and has generally been accepted for a long time in copolymerized or short-chain branched polymers (compare for

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example the electron microscopic pictures presented by Michler [4] or in the work of Minick et al. [5]). But recent works, in particular observations with atomic force microscopes [6,7], now indicate that the blockiness in crystal lamellae is not a peculiarity of non-perfect chains, but most probably a general phenomenon. As it appears now, it is a consequence of a multiple stage route generally followed in the formation of polymer crystallites [8,9]. Given the blocky substructure of the lamellae, block slips provide an easy process for plastic deformations. If there exist a sufficiently large number of independent slip modes, and each block provides three slip planes with two slip directions for each one, it becomes possible to realize any external deformation. In fact, one finds examples in the literature which show these block motions directly, for example, in an earlier work of Yang and Geil [10] on deformed poly-1-butene, where transmission electron micrographs show the blocks and their motion, and now in a recent study by Godehardt et al. [11], who used the atomic force microscope during the deformation of polyethylene.

If block slips represent the dominant general mechanism of yielding up to the point of fibril formation, one would expect to observe these motions not only during large deformations but also in the linear response regime in measurements of the dynamic Young's modulus. A contribution of block slips to the dynamic mechanical behavior in the linear range is, of course, not a new idea. It was raised some time ago, may be at first by Iwayanagi [12], and then also by Takayanagi [13], who assigned one part of the α -process in polyethylene to this kind of motion. In polyethylene the process is superposed by a second part which is, according to a common view, controlled by single chain diffusions through the crystallites, rather than a block motion [14]. Both the block motion and the single chain diffusion enable further deformations of the amorphous interlamellar regions to be realized when they become activated. In s-PP chains are fixed within the crystallites and cannot carry out longitudinal diffusions, but block slips can still exist. We therefore searched in s-PP for the occurrence of block slips in linear response and, indeed, found a process with corresponding properties. As is reported in this paper it can be observed at elevated temperatures. We determined the relaxation rate of the process and found an unusual temperature dependence, qualitatively different from both, Arrhenius- and WLF-behavior, but as we think, conceivable for block slips.

2. Experimental

In the investigations we used a commercial sample of s-PP which was kindly supplied by Fina Oil and Chemicals (Brussels, Belgium). As indicated by ^{13}C NMR, it has 81% of syndiotactic pentades. Frequency- and temperature-dependent dynamic mechanical measurements were carried

out with the DMTA MKII of Polymer Laboratories, covering the frequency range from 10^{-1} to 10^2 Hz and using temperatures from ambient to 110°C . In the dynamic measurements, samples were kept under a constant force of 0.5 N which produced a pre-strain of less than 1% at all temperatures investigated. The amplitude of elongations in the oscillations was set at a constant value of $16\ \mu\text{m}$ corresponding to strains in the order of 0.1%. For completion we also carried out in the neighboring Freiburg Material Research Center some measurements with the Solid Analyzer II of Rheometrics, thereby extending the frequency range down to 10^{-2} Hz.

Crystallinities were deduced from the heat of fusion, determined by a Perkin Elmer DSC4, assuming for the ideal value of a completely crystallized sample $\Delta H_{\text{id}} = 183\ \text{J g}^{-1}$.

For a further characterization of the mechanical properties we prepared an anisotropic sample. A film was drawn at 90°C to an extension $\lambda = 5$. The orientation of the sample was characterized by WAXS and small angle X-ray scattering (SAXS), employing for WAXS an image-plate registration and for SAXS a Kratky camera with slit-like primary beam working at a Cu $K\alpha$ -anode.

3. Results and discussion

Fig. 1 shows the frequency dependence of the real part E' of the Young's modulus measured at various temperatures during a stepwise heating from room temperature to 110°C . The sample was isothermally crystallized at 95°C , annealed at 110°C , and then cooled slowly. As determined by DSC, the crystallinity was 0.25 after the completion of the isothermal crystallization and then during cooling increased somewhat, reaching finally at ambient temperature a value of 0.28. A look at the curves shows two noteworthy features. First, one observes a pronounced drop of E' with temperature. It appears impossible to relate it to a small change in the crystallinity. What we find here is an explicit temperature dependence. An explanation has already been given in our first paper which dealt with the mechanical properties of s-PP [3]. In a situation where the crystallinity remains essentially constant, a drop in the stiffness indicates, generally speaking, a change in the modes of force transmission or more precisely speaking a change in the mechanical coupling of the force-transmitting rigid crystalline objects. In our understanding, these are the blocks which comprise the lamellar crystallites. We therefore consider the decrease in the Young's modulus with increasing temperature as being due to a weakening of the contact forces between the blocks, following from a mobilization and may also be an extension of the non-crystalline regions separating adjacent blocks in the lamellae.

Secondly, one finds always, for all temperatures, an increase in E' with the frequency. For 60°C this increase is linear, but for low temperatures and high temperatures

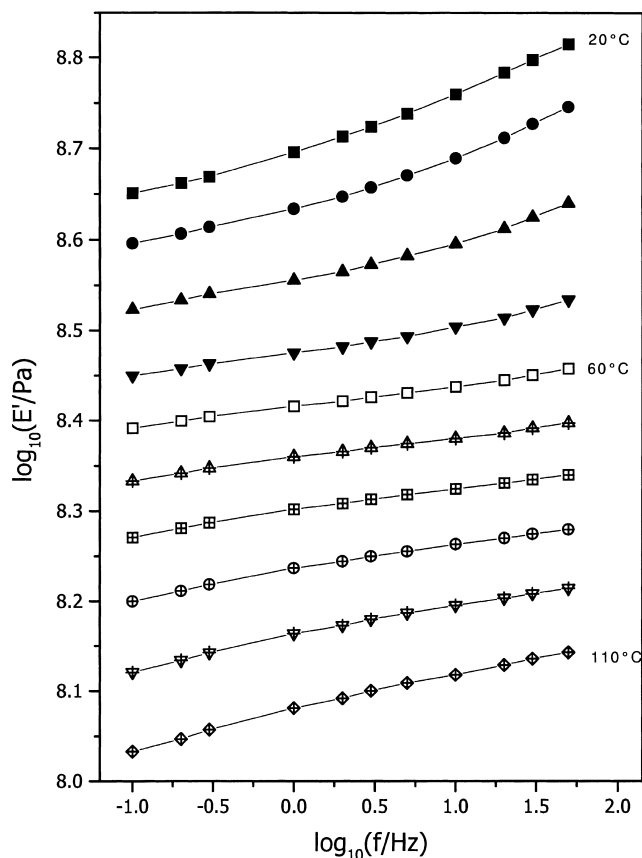


Fig. 1. s-PP, isothermally crystallized at 95 °C, annealed at 110 °C, and cooled to room temperature: Young's modulus (real part) as a function of frequency, measured at the indicated temperatures during a stepwise heating.

one finds characteristic deviations. The measurements at the lowest temperatures show an upward curvature at the high frequency end. Its origin is obvious, as being caused by the dynamical glass process. The new feature comes up at the highest temperatures where the frequency dependence of the Young's modulus shows a downward curvature on decreasing the frequency. The behavior is indicative of an approach to another relaxation process which is slower than the dynamical glass transition. For semi-crystalline polymers the occurrence of such a process, located at the high temperature or low frequency-side of the glass transition, is an often observed phenomenon [15]. If it is observed, the dynamical glass transition is conventionally addressed as β -process and the additional slower process then as α -process. To our knowledge, so far there are no reports about the occurrence of such a process in s-PP. As we see now, it exists, as is indicated by Fig. 1, and further results will be presented later. Following convention, we shall refer to it also as an ' α -process'.

Figs. 2 and 3 show the results of the same experiment in terms of the loss tangent, $\tan \delta$, split up into two ranges, the temperatures below 60 °C which are affected by the β -process, and the higher temperatures above 60 °C, where the influence of the α -process comes up. The

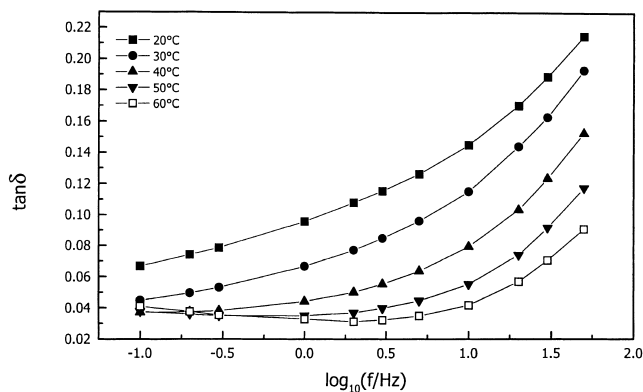


Fig. 2. s-PP, same sample as in Fig. 1: frequency dependent loss tangent measured at the indicated temperatures during a stepwise heating up to 60 °C.

existence of the α -process is demonstrated rather clearly. As it appears, for 110 °C the loss maximum is just reached at the lowest frequency. An even more convincing proof for the occurrence of an α -process is shown in Fig. 4. It represents a master curve composed of the single measurements at different temperatures in Fig. 3 after appropriate shifts along the $\log f$ -axis, i.e. in horizontal direction only. The curve refers to the relaxation behavior at 60 °C; all the curves given in Fig. 3, measured at higher temperatures, were shifted to lower frequencies to produce overlap. As one notes, the construction works perfectly. One obtains a smooth curve representing a relaxation process with a maximum at the lower frequency end at $f = 10^{-3.5}$ Hz.

While carrying out the shift, the uprise on the high frequency side towards the β -process obviously do not fall on a common line. This means that the shift factors for the α -process and the β -process differ from each other. Just as for the α -process, one can also try to establish a master curve for the β -process. The result obtained is shown in Fig. 5. This master curve is now constructed from the curves given in Fig. 2. We choose again 60 °C as the reference temperature.

The master curve shows that although the construction

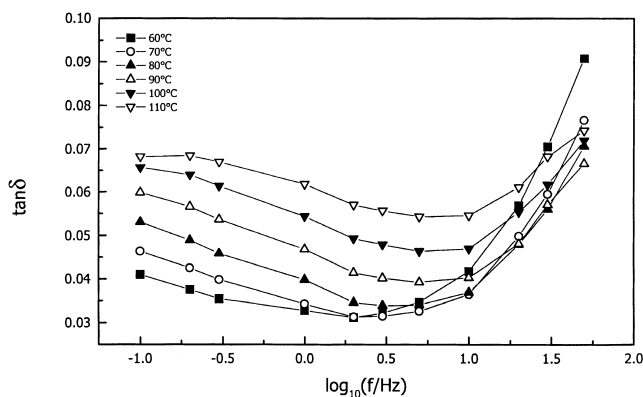


Fig. 3. Frequency dependent loss tangent measured during further heating up to 110 °C.

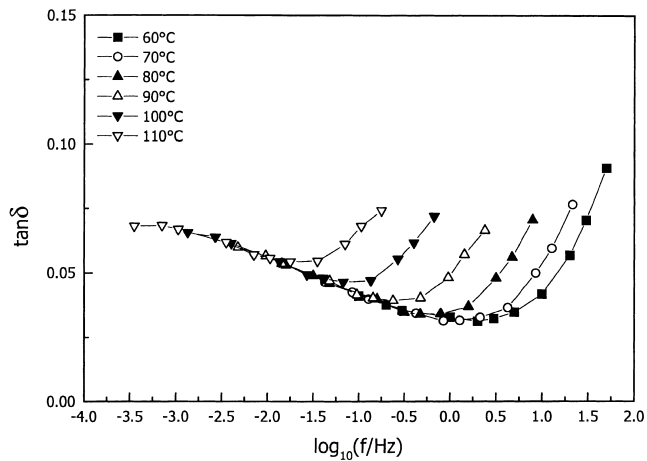


Fig. 4. Master curve constructed from horizontal shifts of the curves in Fig. 3 until an overlap in the low frequency range. The curve for 60 °C is kept at its place.

seems to work at the high frequency end, deviations are found in the intermediate frequency range. They indicate the occurrence of further contributions to the relaxation behavior, but different from the α - and β -processes, its strength is temperature dependent. It is absent at higher temperatures, 50 and 60 °C, but emerges at low temperatures. Hints about its possible origin can be found in publications of Lu and Cebe [16], Schick et al. [17], and Schwarz et al. [18]. For many semi-crystalline polymers, it is found in DSC measurements that the stepwise increase in the specific heat at the glass transition is smaller than expected on the basis of the crystallinity derived from the heat of fusion. The finding indicates that not all of the non-crystallized materials achieve at the glass transition already the full fluid-like mobility. The result is usually expressed by introducing a third ('rigid amorphous') phase which, although non-crystalline, has a greatly reduced mobility. Lu and Cebe for poly(ethylene terephthalate) and Schick et al. for samples of polycarbonate and poly(3-hydroxybutyrate) showed, employing temperature modulated DSC that this

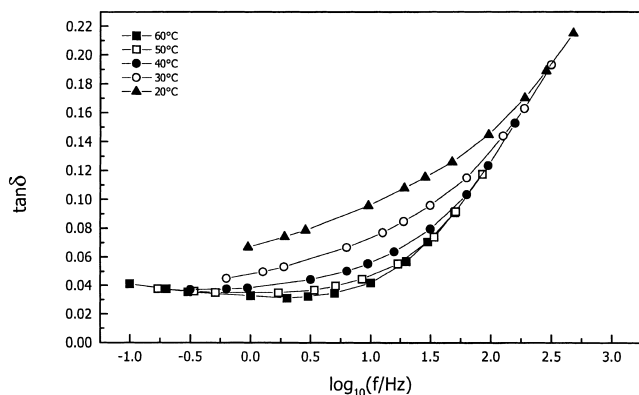


Fig. 5. Master curve constructed from horizontal shifts of the curves in Fig. 2 until an overlap in the high frequency range. The curve for 60 °C is kept at its place.

phase becomes mobilized during the heating process. Schwarz et al. in studies of s-PP found out that this mobilization has in fact a mechanical effect, leading to a drop in the stiffness. We therefore feel that the temperature-dependent contribution in the intermediate part of the loss tangent could well arise from this effect. At low temperatures the third phase with reduced mobility shows up as a contribution at the low frequency wing of the β -process which then disappears on heating.

It is another interesting observation that the construction of the master curve which works so perfectly for the loss tangent cannot be applied to the real part of the Young's modulus. Fig. 6 results when the same shifts as for the loss tangent, different ones for the high and low temperature region, are carried out for E' . The explicit temperature dependence of its magnitude is not at all removed. What does this mean? The answer is simple [19] and leads us also to another conclusion. The loss tangent expresses a ratio between the stored and dissipated energy. If both the stored and the dissipated energy refer to the amorphous regions only then the ratio becomes independent of the crystallinity and of the coupling conditions active between the blocks. Both the α - and the β -processes produce shear deformations of the amorphous interlamellar regions. For the β -process this takes place with essentially rigid lamellae. The α -process then leads to a further deformation. It is mediated by the block slips which cause a further deformability of the lamellae.

Next, we have a look at the shift factors. These are shown

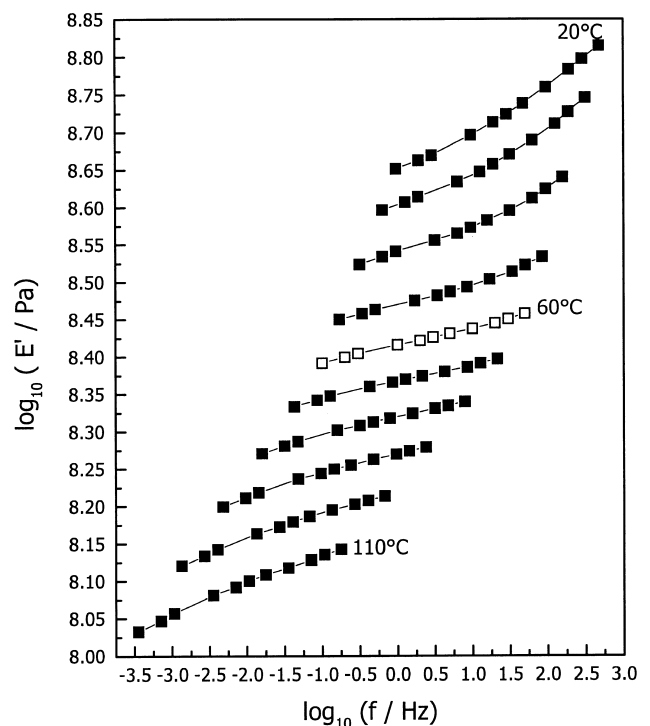


Fig. 6. Result of applying the shifts performed in the construction of the master curves in Figs. 4 and 5 on the curves in Fig. 1.

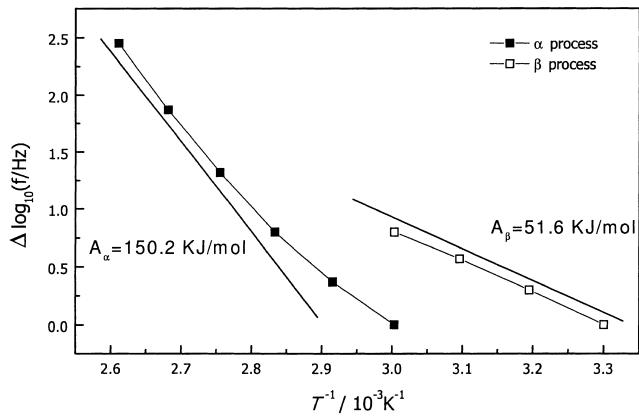


Fig. 7. Shift factors $\Delta \log f$ used in the construction of the master curves in Figs. 4 and 5.

in Fig. 7 for both the β - and the α -processes. For the β -process, we obtain in the limited temperature range a quasi-Arrhenius behavior, but the high activation energy indicates that we deal here with an apparent value which would increase on further approaching the glass transition temperature. The finding for the α -process is of interest. We find an even larger slope in the Arrhenius diagram, corresponding to a huge apparent activation energy. In addition, a curvature which is not that of a WLF-curve, going just the other way round, is noteworthy. One observes an acceleration of the relaxation process with increasing temperature, rather than an increasing retardation with a decreasing temperature as in the WLF-case. Indeed, such a behavior is expected for block slips if the contact forces between the blocks in the lamellae are weakened when the sample is heated. This could arise from a softening of the lateral surfaces of the crystal blocks, so that grain boundaries existing at low temperatures are transformed into fluid-like interblock regions, or a mobilization and growth of the latter ones.

A determination of the temperature dependence of the relaxation rate of the α -process is, of course, better than the knowledge of the shift factors alone. To achieve it, we have to pick up the location of the relaxation maximum for some temperatures. Using the Rheometrics Solid Analyzer, we were successful, and Fig. 8 shows the results. The expansion of the frequency range to lower values carries us over the loss maximum. Using the relaxation rates thus determined at three high temperatures together with the shift factors already measured for the lower temperatures yields the temperature dependence of the frequency at the α -process, shown in Fig. 9. Again, we observe the characteristic upward curvature related with an increase in temperature.

Hence, we have a clear evidence for the existence of an α -process in s-PP at the high temperature side of the dynamical glass transition. The temperature dependence of the relaxation rate is at first unusual, but looks conceivable when we assign the process to block slips. In any case,

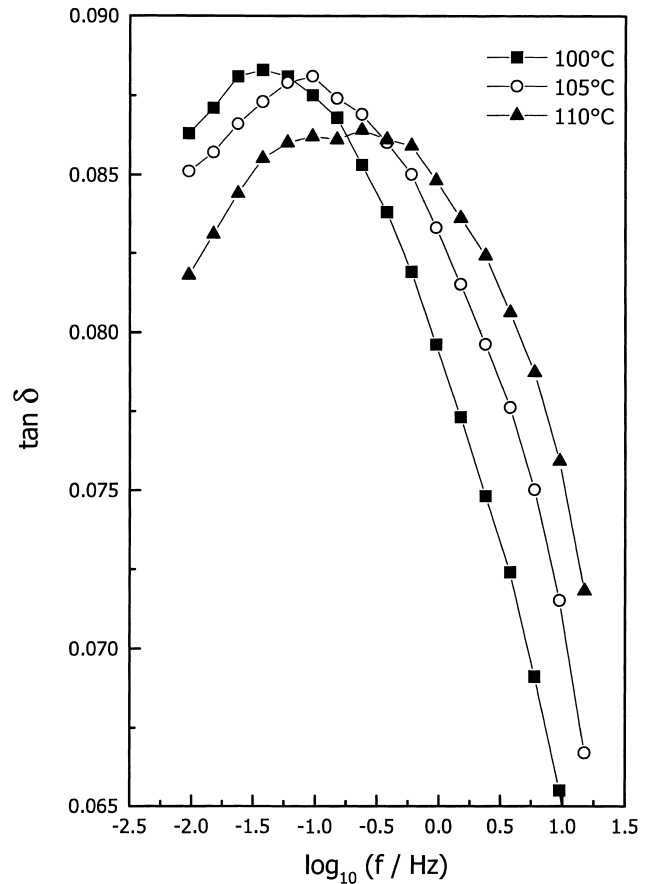


Fig. 8. s-PP, isothermally crystallized at 95 °C and annealed at 110 °C: frequency dependent loss tangent obtained with the Rheometrix Solid Analyzer at the indicated temperatures.

independent of this tentative assignment it is obvious that the α -process produces a second further deformation of the amorphous regions, in addition to that produced at the glass transition. It becomes activated together with a second

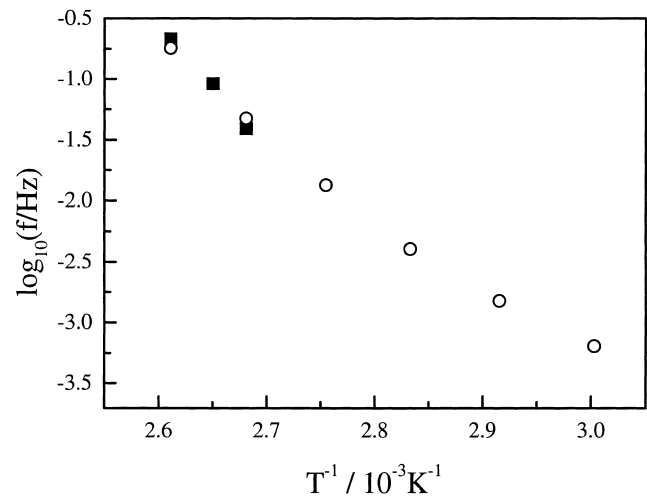


Fig. 9. s-PP, isothermally crystallized at 95 °C: temperature dependence of the relaxation frequency of the α -process following the results shown in Figs. 7 and 8.

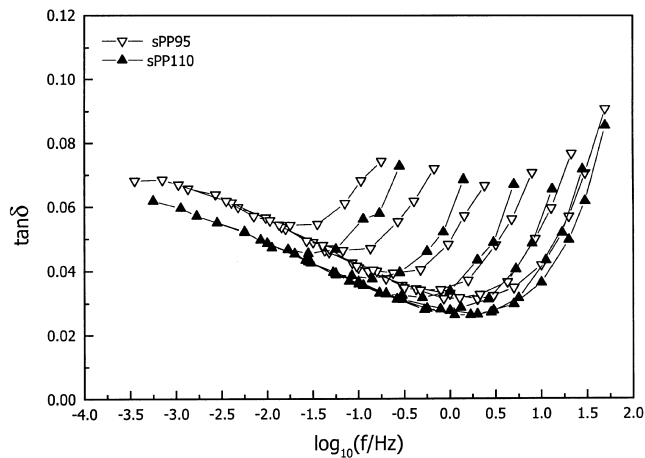


Fig. 10. Two samples of s-PP, isothermally crystallized at 95 and 110 °C: master curves representing the respective α -processes at 60 °C.

retarded response of the assembly of the crystalline parts in the structure.

In order to check the assignment we carried out two further measurements:

- (i) It is possible to vary the crystallite thickness by the choice of the crystallization temperature, and thus in a well-defined way. For block slips one expects an effect, namely a retardation of the α -process with increasing crystal thickness.
- (ii) As was demonstrated in particular by Ward [20] in numerous studies carried out primarily for polyethylene, measurements on oriented samples can be used to analyze the orientational properties of relaxation processes. This often helps in the assignment, and we followed this route.

Figs. 10 and 11 show the thickness dependence of the relaxation processes in s-PP. We compared the relaxation properties of two samples, one crystallized at 95 °C and the other at 110 °C. We know from our previous work [3], where we also carried out SAXS measurements, that the

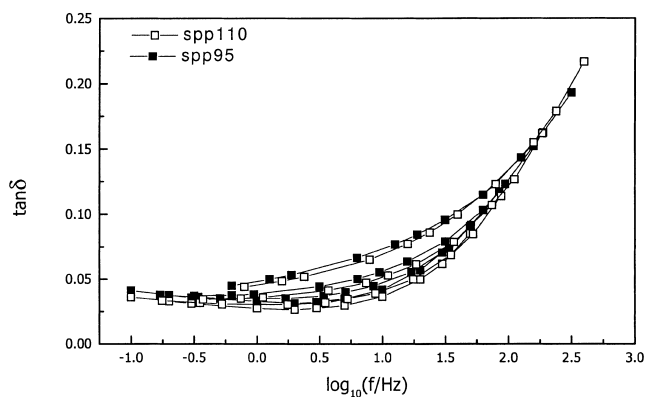


Fig. 11. s-PP, same samples as in Fig. 10: master curves representing the β -processes at 60 °C.

structure parameters at these temperatures are as follows:

$$T_c = 95 \text{ °C} : d_c = 4.3 \text{ nm}, L = 14.3 \text{ nm}$$

$$T_c = 110 \text{ °C} : d_c = 5.6 \text{ nm}, L = 18 \text{ nm}$$

Note that although the length scales of the structures are different, both have the same linear crystallinity, $\phi_l = 0.30$ (which is above the mass fraction crystallinity determined by DSC, an indication for the presence of amorphous regions within the lamellar crystallites). With regard to the effect of the crystal thickness one finds a difference between the β - and the α -processes. There is no effect at all for the dynamic glass transition; however, a retardation of the α -process of the thicker crystals relative to the thinner ones occurs. Even clearer than the results in Fig. 10, which could be either addressed as a shifting towards lower frequencies for the thicker crystals or as a decrease in the magnitude of the loss tangent, is the plot of the shift factors for the two samples shown in Fig. 12. Here, the change in the relaxation rates is obvious.

The anisotropy studies were carried out for the oriented sample. The texture achieved by the drawing process can be seen in the WAXS diagram of Fig. 13. The drawing- and chain-direction is indicated by the arrow. In order to see also the orientation of the lamellae we measured the SAXS curves with a Kratky camera, and the results are shown in Fig. 14. One curve was measured with the slit-like primary beam perpendicular to the drawing direction (0°) and the other parallel to it (90°). The results are indicative of a two-point scattering pattern, i.e. the existence of lamellae with normals parallel to the drawing direction. Fig. 15 shows the frequency dependence of E' at 90 °C for three different samples. They were all cut out of the oriented film, rectangularly shaped, with the long side, along which the tensile stress was applied, chosen in three different directions, parallel and perpendicular to the drawing direction, or inclined at an angle of 45°. At first we note that the values of E' clearly differ between the three samples which demonstrates the global anisotropy in the stiffness of the sample.

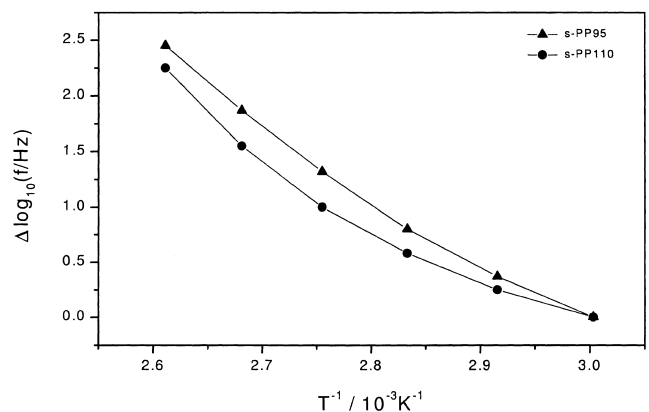


Fig. 12. Shift factors used in the construction of the two master curves in Fig. 10.

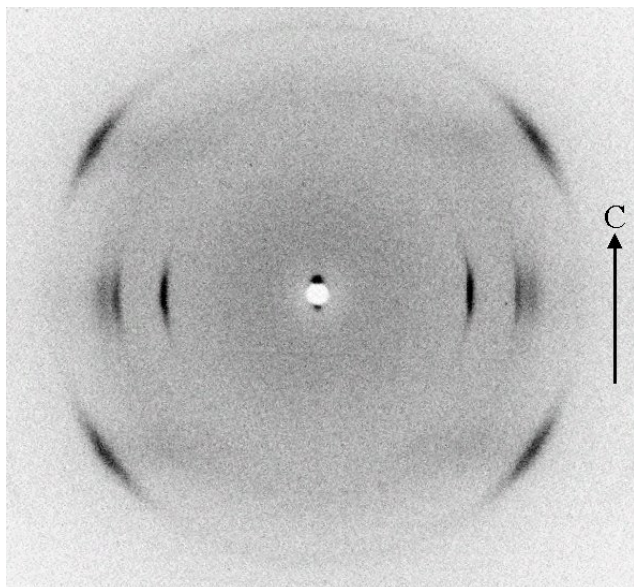


Fig. 13. Oriented film of s-PP, produced by an uniaxial drawing to $\lambda = 5$ at 90 °C: WAXS diagram. The arrow indicates the drawing direction.

On the other hand, the decrease in E' with decreasing frequency, caused by the activity of the α -process, does not show much variation. The relaxation strength, which shows up in the decrease, is apparently very similar for the 90 and 45°-sample and, maybe, slightly smaller for the 0°-sample. Which conclusions can be drawn from the observations? The global anisotropy with a minimum stiffness for the 45°-sample is caused by the β -process. For frequencies above that of the dynamic glass transition one would expect agreement between all the three samples (chains in crystalline s-PP have a helical confirmation, and the crystallites then possess internally only a small mechanical anisotropy [21]). The largest drop introduced by the β -process occurs for 45° because the resolved shear stress acting along the lamellar surfaces then takes on its maximum value. On the

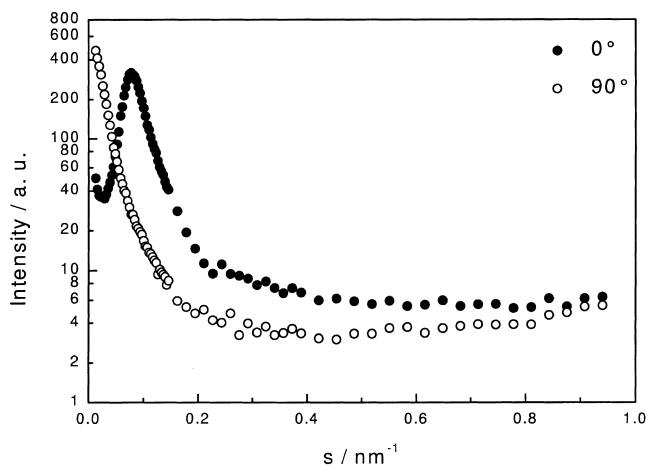


Fig. 14. Oriented film of s-PP: SAXS curves measured with a Kratky-camera with the slit perpendicular (0°) and parallel (90°) to the drawing direction.

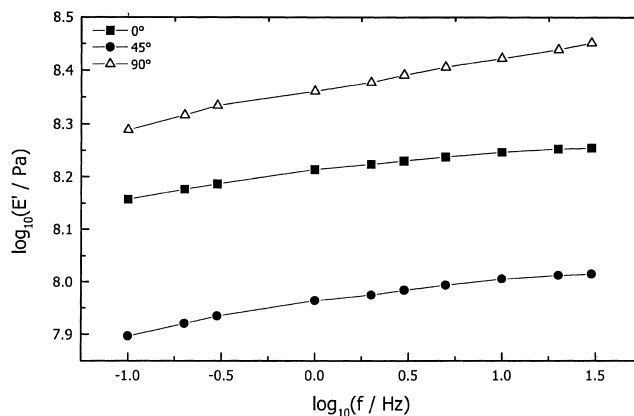


Fig. 15. Samples cut out of the oriented film with the long edge parallel (45°), and perpendicular (90°) to the direction of drawing: frequency dependent Young's modulus showing the orientational dependence of the mechanical properties.

other hand, block slips are much less directionally restricted. There are no restrictions with regard to the slip direction, and this goes together with an isotropic distribution of the block surface planes. For this reason one expects for a block-slip mediated relaxation process not much anisotropy, which would agree with the observation.

4. Conclusions

In conclusion, we have shown the existence of a relaxation process at high temperature or low frequency side of the dynamic glass process in both isotropic and oriented s-PP films. Due to the fact that the molecular chains of s-PP inside the crystallites are fixed, we assign this high temperature relaxation as the intralamellar block motions. This assignment finds support in the unusual temperature dependency of relaxation frequency, the retardation of the process accompanying a crystal thickening and the isotropy of the associated mechanical relaxation strength in an oriented sample.

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