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# A MODULATED DSC STUDY ON THE STRESS OSCILLATION PHENOMENON IN A SYNDIOTACTIC POLYPROPYLENE

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## Abstract

The static loading-induced stress oscillation (SO) in syndiotactic polypropylene (sPP) was studied by modulated differential scanning calorimetry (TMDSC). Samples were taken from the initial necked, premature and mature SO oscillation ranges, respectively, and the related calorimetric responses were compared to those of the bulk material. It was established that necking caused some decrease in the crystallinity. In addition, necking resulted in cold crystallization that was assigned to a polymorphic transition (from all-trans to helical conformation) based on literature results. The TMDSC response was practically the same for necked samples with and without SO. A model was proposed to explain SO. The model assumes the presence of a network (similar to that of semicrystalline thermoplastic elastomers), which is highly stretchable and fails by sudden voiding at the intersections of shear micro bands intermittently.

**Keywords**: modulated DSC, stress oscillation, syndiotactic polypropylene (sPP)

## Introduction

Stress oscillation (also termed strain or self oscillation) was often observed in the necking stage of amorphous but crystallisable polymers. Stress oscillation (SO) means that the necking stress is no longer constant under certain conditions (which are less known) but shows a periodic fluctuation in time (e.g. [1–3]). The oscillation amplitude is rather constant and it is characteristic for the polymer. SO is accompanied by the onset of a striation pattern composed of repeated transparent/opaque bands which are oriented perpendicular to the loading direction. Each stress oscillation generates one transparent/opaque band. The opaque bands are usually voided and crystalline (e.g. [4]). The most widespread explanation for SO is based on

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strain-induced crystallization: the stress increase is given by strain (work) hardening whereas its sudden drop is owing to crystallization (release of the crystallization heat). Accordingly, strain–induced cold crystallization is believed to be the cause of SO. The scenario is, however, not so simple especially under spot of some new findings. SO can be produced also in amorphous polymers which do not undergo strain-induced crystallisation, such as polyvinyl chloride and polycarbonate [5]. On the other hand, SO phenomenon was recently observed in syndiotactic polypropylene (sPP) [5–6] which is of semicrystalline nature. One should note that SO was produced also in another semicrystalline polymer, viz. trans-polyisoprene, however, the authors did not recognize and discuss this phenomenon that time [7]. A further peculiarity with sPP is that SO has been triggered at room temperature (RT), i.e. above the glass transition temperature ($T_g$) of this material. Note that until now SO was mostly observed in amorphous (co)polyesters when loaded below their $T_g$ [8]. In order to deduce a general theory for SO these new results should be taken into consideration. Aim of this work was to contribute to some open issues of SO by comparing the calorimetric response of sPP with and without stress oscillation. Major emphasis was put on the question whether or not strain-induced crystallization is a key aspect in sPP.

## Experimental

Object of this study was an sPP grade (EOD93-07) of Fina Oil and Chemical Co. with the following molecular characteristics: $M_w$=170 kg mol$^{-1}$, $M_w/M_n$=3.7. Its stereoregularity based on the syndiotactic sequences (racemic pentad content, rrrr) measured by $^{13}$C–NMR was 79%.

0.6 mm thick sheets were produced from the sPP granules by hot pressing. The press cycle included a melting at $T$=190°C followed by cooling to $T$=80°C where isothermal crystallization was performed for ca. 20 min prior to cooling further to room temperature (RT).

Rectangular specimens (width: 10 mm) cut from the sheets were subjected to tensile loading (clamping length: 70 mm) at RT by step-wise increase of the deformation rate [5]. To introduce necking the deformation rate was initially set for 2 mm min$^{-1}$ and then increased for 50 mm min$^{-1}$. This change in the deformation rate resulted in a sudden rise/drop in the stress as obvious in Fig. 1. Figure 1 displays the stress-strain (σ–ε) curve of the sPP specimen studied. This figure also shows the SO in its mature phase more detailed.

Samples for TMDSC were taken from the bulk (gripped area of the specimen), from the initially formed neck, from the premature and mature (well developed) SO ranges (Fig. 1). TMDSC investigations were performed on a TA Instruments Thermal Analyst 2200 System as described in our previous works (e.g. [9–10]). In this study a heating rate of 2°C min$^{-1}$ was used with a modulation amplitude of ±0.318°C min$^{-1}$ and a modulation time of 60 s were selected.

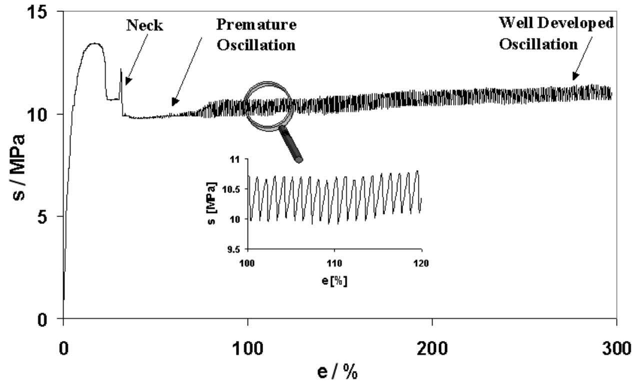

**Fig. 1** Stress oscillation (SO) in the stress-strain (s-e) curve of an SPP specimen due to static tensile loading. Note: this Fig. indicates the positions of the TMDSC sampling

## Results

### *Necking and striations*

The striation bands are not transparent/opaque but less white/more white in sPP. Their onset is accompanied by the usual surface undulations. This can be well assessed by a laser profilometer (Fig. 2). The 3-dimensional 'roughness' plot indicates that the spacing between the surface undulation (i.e. striations) is quite small (ca. 0.4 mm). The fine spacing of the SO bands already suggests that the TMDSC results can hardly be assigned to either a less or a more whitened band. As a consequence, the TMDSC traces represent the 'average' calorimetric response of the related neck section of the specimen. Scanning electron microscopic (SEM) pictures taken from the mid section of the necked sPP clearly reveal that the surface undulation pattern is caused by an intermittent voiding process (Fig. 3). So, the formation of the more white bands following the less white ones (inherent colour of the sPP) can be explained by either crystallization and/or by light scattering caused by the voids generated. These findings are in harmony with the literature [4, 5, 8].

### *TMDSC results*

Figure 4 displays the conventional (C), reversing (R) and non-reversing (NR) TMDSC traces taken from the bulk sample. One can recognize on the R and C traces that the sPP starts to melt very early. This suggests that the sPP crystals exist in several populations of various perfection and thus of various thermal stability. Such behaviour is easy understandable by considering the moderate stereo- and regioregularity of the sPP used. During heating the less perfect crystals become more perfect by a subsequent melting/recrystallisation process. The deviation in the base line of the NR trace up to ca. 100°C (Fig. 4) seems to corroborate such an assumption. The bulk material shows a double melting peak at $T\approx 115$ and $\approx 130$°C, respectively

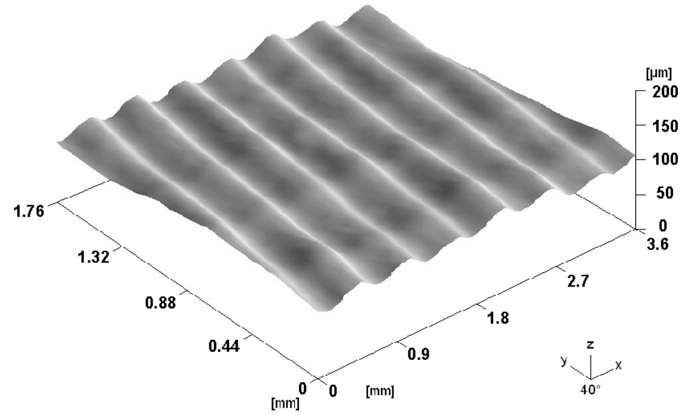

**Fig. 2** 3-dimensional contour plot on a section of the necked sPP specimen from the mature stress oscillation range, Note: image was captured by a laser profilometer (UBM Messtechnik, Ettlingen, Germany)

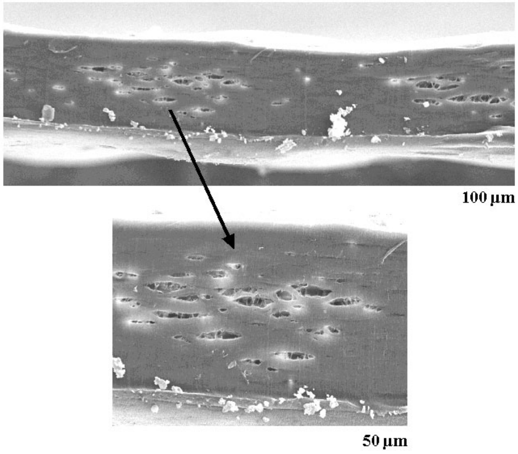

**Fig. 3** SEM pictures taken from a through thickness section of the necked specimen in the well developed stress oscillation range. Notes: specimen was cut through the thickness of the necked specimen along its mid section; the surface undulations caused by repeated voiding is well resolved; pictures taken by a Jeol JSM 5400 microscope after sputtering the specimen surface with Au/Pd alloy

(C and R traces in Fig. 4). The reason behind this peak doubling is definitely a recrystallisation process as indicated by the crystallization peak in the NR curve. Doubling (or even tripling) of the major melting peak in sPP was often observed and it was attributed to the formation of more and less stable (perfect) crystals produced during isothermal crystallization [11].

The TMDSC response of the necked region differs markedly from that of the bulk – compare the related traces in Fig. 4 and 5. First, no dual melting peak is present in the neck. Second, the melting enthalpy – according to the R and C traces – is considerably re-

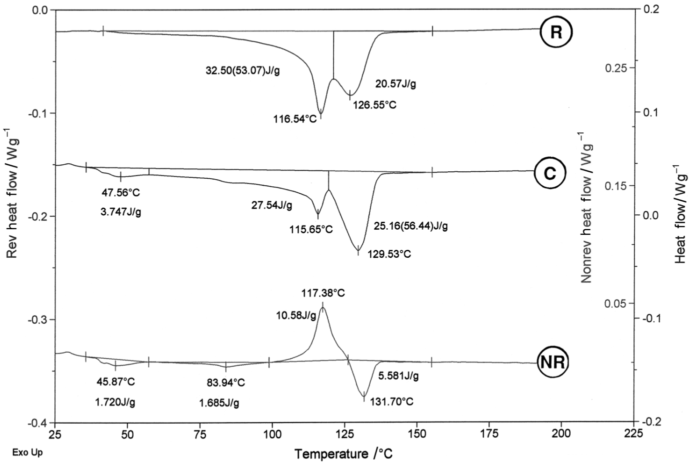

**Fig. 4** TMDSC curves for the bulk (non-stretched) sPP. Designations: C-conventional, NR-non-reversing and R-reversing components, respectively

duced due to necking when compared to the bulk. Third, and the most striking difference is the onset of a pronounced broad cold crystallization peak at $T\approx 70°C$. This cold crystallization peak is well resolved in the C, and especially in the NR traces. The large difference between the cold crystallization ($T\approx 70°C$) and recrystallisation peak ($T\approx 118°C$) suggests that the former one should be related to the crystallization of a polymorphic modification that was generated during necking (plastic deformation). If it is so, then the TMDSC response of the samples taken from the SO region should be similar to that of the initial necking. Comparing the TMDSC traces of samples taken from the premature (Fig. 6) and well developed stress oscillation (Fig. 7) no substantial difference can be identified. In addition, the overall TMDSC response from the SO regions is quite similar

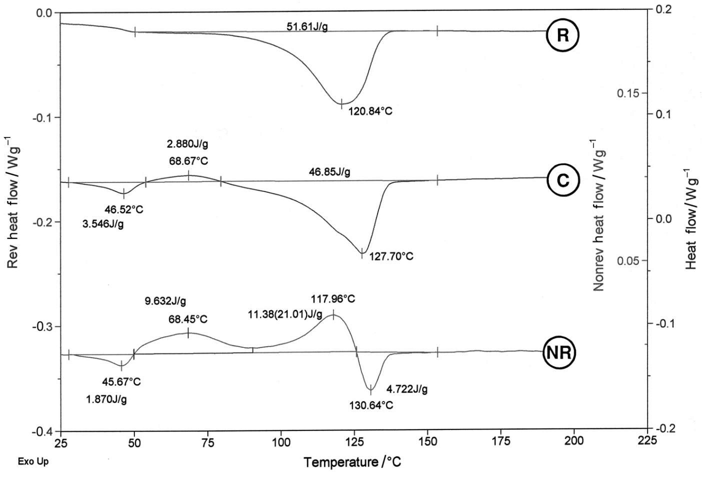

**Fig. 5** TMDSC curves from the necked region (Fig. 1) of the sPP specimen. For designations Fig. 4

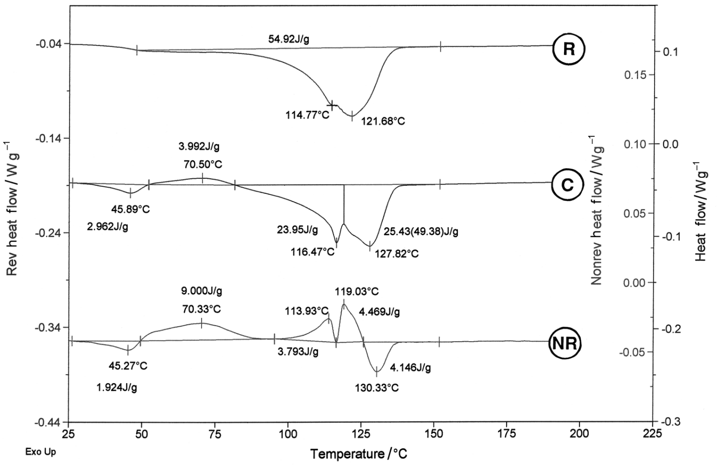

**Fig. 6** TMDSC curves from the premature SO region (Fig. 1) of the sPP specimen. For designations Fig. 4

to that of the neck (Figs 5 to 7). However, there are some differences. First, the double melting reappears in the SO stage (C and R signals in Figs 4 and 6). Second, the NR trace in Fig. 6 shows a double crystallization peak at $T≈120$°C which is not present in any other samples (Figs 4 to 7). The latter may indicate the presence of 3 populations of crystallites melting above 100°C. Nevertheless, one can still claim that the overall melting and thus crystallinity of the stress oscillated sPP is less than that of the bulk. Further, the cold crystallization peak at $T≈70$°C shifts toward slightly higher temperatures according to the ranking: neck ≈ premature SO < well developed SO. Practically the same ranking holds for the enthalpy of this peak (NR traces in Figs 5 to 7). The dual recrystallization peak at $T≈110$°C (NR trace in Fig. 6) may be a hint for the formation of stable and thus at high

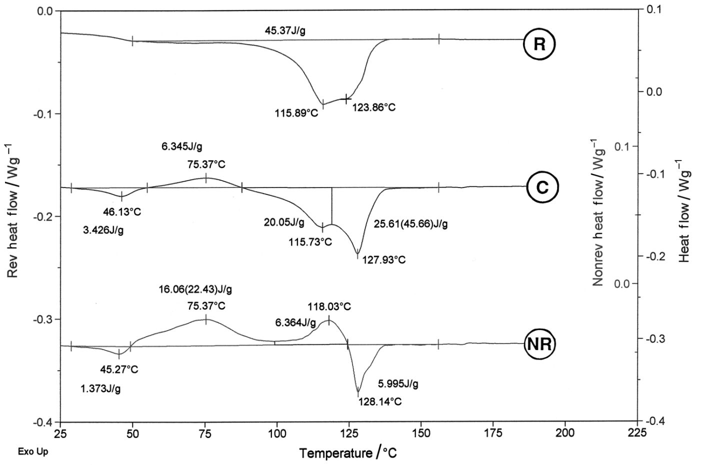

**Fig. 7** TMDSC curves from the well developed SO region ( Fig. 1) of the sPP specimen. For designations Fig. 4

temperature melting polymorphic modifications. It should be noted that the above TMDSC findings differ basically from those published by Loos *et al.* [12], which is the only TMDSC study on sPP according to the authors' knowledge so far.

## Discussion

sPP, similarly to isotactic polypropylene (iPP), exists in several polymorphs due to various possible chains packing in the crystalline cells (e.g. [13–15]). sPP crystallizes in its most stable form characterized by a 2-fold helical conformation $(TTGG)_n$, when cooled from the melt. Drawing below or beyond the $T_g$ is accompanied by a crystal-crystal (polymorphic) transition from helical toward trans planar conformation $(TTTT)_n$ (e.g. [16–18]). This metastable polymorph is termed also planar zigzag or all-trans conformation. The cell packing of the all-trans version is more dense and its calculated crystallographic density is therefore higher than that of the helical polymorphs (for which different values are published). As a consequence, the helical to all-trans transition should be accompanied by volume contraction. Volume contraction is compensated by voiding in a uniaxial tensile test. Accordingly, the onset of voiding may be traced to this crystalline transition at least in an sPP of sufficiently high crystallinity. The latter is not valid, however, for our sPP when considering its crystallinity (note that 207 J $g^{-1}$ was deduced for a 100% crystalline sPP [19]). So, the crystalline transition alone can hardly explain the voiding observed and even less its intermittent feature (Figs 2 and 3). On the other hand, the TMDSC data clearly indicated some crystallinity decrease due to SO. Accordingly, for the appearance of the more whitened striations bands voiding should be made responsible. Further, the TMDSC response of the necked samples less depends whether or not SO occurred. The marked cold crystallization at $T\approx 70°C$ owing to necking or necking superimposed by SO may be rendered to the crystalline transition from all-trans (produced by necking) to helical conformation (which are thermally more stable) [18]. The melting/recrystallization processes at high temperature ($T$=110°C) should be related to transitions between helical polymorphs. It is the right place to call the attention to the low temperature melting peak at $T$=46°C that can be found in the NR and C but never in the R signals of the sPP samples (Figs 4 to 7). This behavior can not be traced to the glass transition (laying at about 0°C) but should likely be attributed to some second order transition between sPP polymorphs. On the other hand, further experimental evidences are needed to substantiate the above supposed polymorphic transitions. The required results could be received using wide-angle X-ray scattering, infrared or Raman spectroscopy. Nevertheless, the basic question is still open: what is the reason of the SO in sPP?

Our model explanation is as follows. Necking, which is the prerequisite of SO in all polymers, creates a stretched entangled network. The 'knots' of this stretched network are given mostly by crystals of all-trans conformation. Recall that this network structure strongly resembles to that of thermoplastic elastomers of semicrystalline type. Such a model was already suggested [16] to explain the elasticity of sPP. As origin of the elasticity the reversible transition between the helical and all-trans modifications was proposed [18]. It is intuitive that the network has some ‘living’ character, i.e. there is a fluctuation in both knots and entanglements during loading. As a consequence this ‘living’ network exhibits some strain hardening feature – this is the explanation for the stress rise in the SO amplitude. The local deformation of this composed network is highly inhomogeneous. This triggers per se the onset of shear deformation. When some small crystals are disrupted (resulting in lower crystallinity as observed) during stretching, the shear deformation is even more amplified (analogy with a fisher net with highly different holes which trigger local shear-type deformations within the net). Intersections of the shear bands (the direction of which is definitely far from the ideal 45°) serve as nucleons of the voiding. When the density of the intersecting shear micro bands reaches a critical value, the material is weakened and its load carrying capacity drops via sudden voiding. This is the explanation for the stress drop in the SO amplitude (SO magnification in Fig. 1). The beauty of this explanation is that intersection of shear bands hardly occurs at the specimen surface. This is in line with the experimental findings as voiding never takes place at the surface but always in the mid section of the specimens (Fig. 3). Based on the above model one can predict that sPP grades of increasing crystallinity and molecular weight (and thus with increasing number of tie molecules) should show more frequent SO (i.e. lower spacing between the striation bands) and larger SO amplitudes than those with lower crystallinity and lower molecular weight. The role of tie molecules in the strain hardening behaviour of sPP was already suggested [20]. Attention should be paid to the fact that this model presumes that all polymers undergoing SO should fail by multiple shear banding, diffuse shear yielding. Fortunately, this is the case according to the authors’ knowledge.

## Conclusions

Based on this calorimetric study performed on the stress oscillation of a sPP, the following conclusions can be drawn:

- TMDSC is a valuable tool to demonstrate the formation and presence of sPP polymorphs. A proper assignment of the TMDSC peaks to the related transitions in the sPP polymorphs requires, however, further independent experimental investigations (e.g. by micro focus synchrotron X-ray radiation, infrared or Raman spectroscopy)
- TMDSC response of necked samples with and without stress oscillation (SO) is similar. Necking favours the cold crystallization of sPP which was traced to polymorphic transition from all-trans to helical conformation based on literature data
- a model was proposed to explain the SO in sPP. The model assumes the presence of a locally stretchable network structure (its strain hardening rises the stress). This network breaks intermittently due to the densification of intersecting shear micro bands. The latter weakens the polymer and causes the stress drop during SO. These intersections are the embryos of the voids generated by SO.

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