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Structures of mono-unsaturated triacylglycerols. IV.
The highest melting $\beta'$-2 polymorphs of trans-mono-unsaturated triacylglycerols and related saturated TAGs and their polymorphic stability

The $\beta'_1$-2 crystal structures of a series of mixed-chain saturated and trans-mono-unsaturated triacylglycerols containing palmitoyl, stearoyl and elaidoyl acyl chains have been solved from high-resolution powder diffraction data, from synchrotron as well as laboratory X-ray sources. The structures crystallized in the space group $I\overline{2}$ with two independent molecules forming a dimer in the asymmetric unit, and packed in double-chain length layers. Unlike the corresponding $\beta$-2 structures the solved $\beta'_1$-2 structures have different molecular conformations for the symmetric and the asymmetric mixed triacylglycerols, both with the $sn$-2 chain in a leg position of the chair-shaped conformation. A transformation to the $\beta$-2 structure with the $sn$-2 chain in the back position is complicated and unlikely to take place in the solid state. A novel $\beta'_0$-2 polymorph of PSS has been crystallized and its structure has been solved. The melting point (239 K) of this so-called $\beta'_0$-2 polymorph is 2 K above that of the $\beta'_1$-2 polymorph and almost equal to that of the $\beta$-2 polymorph of PSS. The difference in packing of the $\beta'_0$-2 versus $\beta'_1$-2 structure explains the slow $\beta'_1$-2 to $\beta'_0$-2 phase transition. The transition is strikingly similar to the $\beta_2$-3 to $\beta_1$-3 transition in cis-mono-unsaturated triacylglycerols.

1. Introduction

Fat blends are used as shortenings in bakery products and in table spreads to provide these products with the appropriate stability, firmness, and melting and crystallization properties. For most applications the mixture of triacylglycerols (TAGs) in the fat blends should be in the $\beta'$ polymorph. The $\beta'$ phase crystallites are small, have a needle-like crystal habit and tend to aggregate into a network, in which air and liquid components are better stabilized than by the larger $\beta$ phase crystallites. As a result, the $\beta'$ phase provides a smooth feel in the mouth (Wiedermann, 1978; Ghotra et al., 2002). Stability of the $\beta'$ phase is important and phase segregation or a transition to the $\beta$ phase should be avoided because of deterioration of the quality of the product. For example, the problem of graininess in margarines due to the occurrence of $\beta$-phase crystallites is well known (Watanabe et al., 1992).

Most vegetable oils are too soft to be applied as such in the above-mentioned consumer products. They need modification, e.g. via fractionation of the natural product (Timms, 2005; Kellens et al., 2007) or interesterification with other, harder types of fat (Sreenivasan, 1978). A third option is (partial) hydrogenation of the cis double bonds that are present in mono-unsaturated oleic acid chains (cis-9-octadecenoic acid: O; one of the most abundant unsaturated fatty-acid chains in natural fats and oils), and other polyunsaturated fatty-acid groups. For example, palm oil and low-melting palm-oil frac-
tions such as palm olein contain large amounts of PPO 
(palmitic acid, hexadecanoic acid: P), POO and POP. These oil
components may be a starting source for the production of β'-
stable PSP (stearic acid, octadecanoic acid: S), PPS and PSS.

Although partial hydrogenation reduces the degree of 
unsaturation, increases the melting point and provides an 
improved stabilization against oxidation, it also allows the
isomerization of the cis double bond into the trans isomer, e.g.
the oleic fatty-acid chain becomes its trans isomer, elaidic acid 
(trans-9-octadecenoic acid; E). An overwhelming amount of 
research has been carried out to assess the potential health 
hazards of these trans fatty acids because of their suspected 
competition with essential fatty acids (Valenzuela & Morgado, 
1999). Generally this research has led to the opinion that trans
fatty acids hold certain health risks, resulting in a strong 
tendency to reduce their amount in food products.

Elaidoyl containing TAGs such as PEP and PPE are 
commonly believed to be structurally similar to their fully 
saturated analogues, PSP and PPS, respectively, although very 
little is known about their actual packing. Fully saturated and 
trans-mono-unsaturated TAGs can crystallize in various 
polymorphs, with melting points that usually increase in the 
order α, β2, β1 and β, but the occurrence and stability of the 
polymorphs depend on the precise fatty-acid composition of 
the TAGs. The existence of both β2-2 and β1-2 has been 
reported for PSP (Gibon et al., 1985) as well as for the trans-
mono-unsaturated TAGs PEP and PPE (Elisabetti et al., 1998), 
while for PSS and PPS only the higher melting β1-2 has been 
reported (Lutton et al., 1948; Lutton, 1950).

Conformational and packing differences influence the 
polymorphic stability and phase transition behavior of the 
various TAGs. To obtain a better understanding of these 
processes, we used DSC and time-resolved X-ray powder 
diffraction (XRPD), together with crystal structure 
determination from the XRPD data. We found evidence for 
the existence of the lower melting β2-2 for PSP and PSS from 
the diffraction data and discovered a novel β' polymorph of PSS, 
coined β2-1, that melts at a higher temperature than the β1-2 
polymorph. In addition to the crystal structure of this novel 
β2-1 polymorph of PSS, we also present the crystal structures of 
the β1-2 polymorphs of PEP, PPE, PSP and PPS.

The structures will be analysed in terms of their methyl end-
plane packing, and compared with the β2 phase structures of 
these and similar TAGs that have been reported in paper III of 
this series (van Mechelen et al., 2008) and a few β'-type crystal 
structures of TAGs that were solved earlier: CLC (single 
crystal), MPM (powder; van Langevelde et al., 2000) and PPM 
(single-crystal; Sato et al., 2001).

2. Experimental

2.1. Samples, sample preparation and data collection

Samples of PEP and PPE have been obtained from Larodan 
Fine Chemicals AB (Malmö, Sweden). Molten sample mater-

Carbon chain lengths are represented by the acronyms S: C18, P: C16 and E: 
C18:1 (trans), respectively.

For PEP, PPE, PSP and PPS XRPD data for structure 
solution were collected at room temperature (298 K) at an 
X’pert Pro MPD diffractometer, equipped with a sealed Cu X-
ray tube, a hybrid monochromator, primary and secondary 
soller slits with 0.01 rad divergence and an X’celerator strip 
detector (PANalytical, Almelo, The Netherlands). The 
continuous scans were binned with a step size of 0.008° 2θ. 
High-resolution synchrotron powder (HR-SPD) data of PSP 
were collected at the synchrotron beamline BM01b at the 
ESRF (Grenoble, France) at 250 K. The continuous scans 
were binned with a step size of 0.005° 2θ. During the data 
collection of PSP, the temperature at the capillary was 
controlled with an Oxford Instruments Cryostream 
(Abingdon, England), mounted with the temperature-
controlled N2 gas stream perpendicular to the capillary. This 
limited the temperature-controlled length of the capillary to 
4 mm.

To determine the melting points (Tm) of the polymorphs and the phase-transition points, time- 
and temperature-
resolved XRPD experiments were carried out using an X’pert 
Pro MPD instrument with an elliptical mirror, primary and secondary 
soller slits with 0.02 rad divergence, an X’celerator 
strip detector and an Oxford Instruments Cryostream for 
temperature control. The latter was mounted with the 
temperature-controlled N2 gas stream being parallel to the 
capillary and with an X-ray transparent cylindrical polymer 
film guiding the stream along the capillary. The capillary 
samples were heated at 0.5 K min⁻¹ and the diffraction 
pattern was monitored continuously in 1 min scans from 0.5– 
30° 2θ with a step size of 0.016° 2θ. Capillaries were spun 
continuously in all experiments. Melting and phase-transition 
temperatures were determined by quenching (−30 K min⁻¹) a 
seed-free melt from ~ 10 K above the melting point of the 
most stable (β') polymorph to 253 K so that the α phase 
crystallizes. Subsequently, the sample was heated slowly at 
0.5 K min⁻¹ and simultaneously the diffraction pattern was 
recorded with a time resolution of one minute. This protocol 
shows the development of the polymorphs: α transforms into 
β2-2, β2-1 transforms into β1 and, finally, heating of the β1-2 
ends in a melt. It should be noted that a higher melting (β-2) poly-
morph of these TAGs exists, but this polymorph is difficult or 
even impossible to obtain from the melt (van Mechelen et al., 
2008).
Phase transitions were analysed with DSC using a Linkam DSC600 instrument (Linkam Scientific Instruments Ltd, Tadworth, England). Samples were heated at 0.5 K min\(^{-1}\) and quenched at \(-30\) K min\(^{-1}\). Although the \(\beta_2^l\) to \(\beta_1^l\) transition process is clearly visible with our time-resolved XRPD equipment, it is not easy to trace with DSC using the same temperature profile.

Phase-transition points and melting points are listed in Table 1. The \(T_m\) of \(\beta_0^l\) of PSS has been determined in a separate XRPD run with \(\beta_0^l\) as the starting phase.

### 2.2. Indexing, model building, structure determination and refinement

As already explained in other publications (van Mechelen et al., 2006a,b), indexing of TAG powder diffraction patterns is not straightforward because of the dominant low-angle and higher-angle zones. The program McMaille (Le Bail, 2004) can generate a list of cell suggestions, provided the search space is limited by applying restrictions to the allowed cell dimensions. With the help of the program Chekcell (Laugier & Bochu, 2001) a further selection and cell refinement could be carried out. Eventually this led to the monoclinic and orthorhombic unit cells that enabled the solution of the \(\beta_2\) structures.

The TAGs discussed in this paper all crystallize in a chair-shaped conformation (Fig. 1). The positions of the three \(sn\)-acyl chains, numbered 1, 2, 3 from left to right in the three-character TAG acronyms, may differ from TAG to TAG and therefore a numerical identifier \([x–y]\) is used to discriminate the conformations. In the notation \([x–y]\) the ‘\(x\)’ is the \(sn\) chain (number) that is in the chair’s back-leg position and the ‘\(y\)’ the \(sn\) chain that forms the seat plus the front-leg position. For symmetric molecules, such as PEP and PSP a \([1–2]\) conformation is equivalent to a \([3–2]\) conformation, but for asymmetric molecules, such as PPE and PPS, the presence of the longer chain at either the back or at the seat/front-leg position, e.g. \([2–1]\) PPE \textit{versus} \([2–3]\) PPE, respectively, imply different structural models with potentially different types of packings.

Fig. 2 shows the diffraction patterns of the \(\beta_2\) structures. The pattern of \(\beta_2\)-PSP has been reindexed to Cu \(K\alpha_1\) radiation to simplify the comparison with the other patterns. The lowest-angle observed reflection in all the patterns (\(d\) spacing \(\sim 43–44\) Å) is indicative of a double-chain length packing and is denoted by the addition of ‘\(2\)’ to the polymorph name.

For the structure solution of the \(\beta_2\) structures with FOX (Favre-Nicolin & Černý, 2002) a starting model with a \([1–2]\) conformation was built in a Z-matrix description. At the start-up of the structure solution process (parallel tempering) rigid molecular models were used with translational and rotational freedom only. In the course of the structure solution process, only torsion angles around the central glycerol moiety were released, one by one.

Structure refinement was carried out with the program GSAS (Larson & Von Dreele, 1987). The background was modelled by a Chebyshev polynomial. By using profile function 4, \((hkl)\)-dependent peak broadening as well as low-angle peak asymmetry was taken into account. Soft restraints were applied to all the distances and angles. Soft planar restraints were applied to the saturated acyl chains (S, P) in the legs and the back of the chair-shaped molecules. Planar restraints were also applied to the carbon acyl chains at either side of the \textit{trans} double bond in the E-chain. Atomic displacement parameters have not been refined. Correction for preferred orientation ([001] as direction) with the March–Dollase function (March, 1932; Dollase, 1986) in the final state of the refinement affected the \(R\) values only slightly. A summary of the results of the Rietveld refinements is listed in Table 2. \(^2\)

### 3. Results and discussion

#### 3.1. Structure determination process

**3.1.1. \(\beta_2\) PEP, \(\beta_2\) PSP, \(\beta_2\) PPE and \(\beta_2\) PPS.** The patterns of \(\beta_2\) PEP, \(\beta_2\) PSP, \(\beta_2\) PPE and \(\beta_2\) PPS could be indexed as monoclinic with eight molecules in the unit cell in view of the expected density of \(\sim 1.0\) g cm\(^{-3}\). The lower-angle part of the fingerprint area of these patterns is dominated by the \((31\ell)\) (\(\ell = \text{even}\)) reflections, while the \((31\ell)\) (\(\ell = \text{odd}\)) reflections are absent (Fig. 3). Also the \((00\ell)\) (\(\ell = \text{odd}\)) reflections are absent, but no other systematic absences are detectable, implying \(I1\)–1 or the non-standard (and related) \(A1\)–1 as possible extinction symbols. Structure determination runs with mirror-plane-containing space groups were not successful, leaving \(I2\) (and \(A2\)) as the possible space group option(s), with two independent molecules in the asymmetric unit.

\(^2\) Supplementary data for this paper are available from the IUCr electronic archives (Reference: DR5019). Services for accessing these data are described at the back of the journal.
Fig. 3 shows that the (31\ell) reflections of \(\beta_1\)-2 PEP and \(\beta_1\)-2 PSP are grouped in pairs with opposite signs for the \(\ell\) values. This pairing also occurs in \(\beta_1\)-2 PPE and \(\beta_1\)-2 PPS, but with unequal \(\ell\) values. With the program Chekcell an alternative indexing in space group \(A2\) was found for \(\beta_1\)-2 PPE and \(\beta_1\)-2 PPS with pairs of equal \(\ell\) values of opposite sign while keeping the (600) at its position. In this alternative \(A2\) cell for \(\beta_1\)-2 PPE as well as \(\beta_1\)-2 PPS [2–3] models could be refined to quite acceptable \(R_p\) values, just above (~1\%) those of the final \(I2\) models. Although the major observed intensities were covered well, discrepancies at minor features, especially at lower angle, led to the conclusion that these alternative \(A2\) models are incorrect.

Eventually, in the space group \(I2\) structural models could be refined for \(\beta_1\)-2 PEP, \(\beta_1\)-2 PSP, \(\beta_1\)-2 PPE and \(\beta_1\)-2 PPS. The [1–2] conformation worked out well for PEP and PSP. In PPE, however, this conformation led to unacceptable bumping problems (i.e. opposing molecules having contact distances which are too short) at the methyl end-plane interface. A [3–2] conformation did not solve this problem and even had an empty space between the aligned \(sn\)-2 chains. Analogous to the single-crystal structure of PPM (Sato et al., 2001), combinations of two PPE molecules with different conformations, [2–1] and [2–3], were tested, but these models were also improbable owing to bumping problems at the methyl end-

**Table 2**
Summary of the results of Rietveld refinement.

<table>
<thead>
<tr>
<th></th>
<th>[1–2](\beta_1)-2 PEP</th>
<th>[1–2](\beta_1)-2 PSP</th>
<th>[2–3](\beta_1)-2 PPE</th>
<th>[2–3](\beta_1)-2 PPS</th>
<th>[1–2](\beta_1)-2 PSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical form</td>
<td>C_{33}H_{60}O_{16}</td>
<td>C_{33}H_{60}O_{16}</td>
<td>C_{33}H_{60}O_{16}</td>
<td>C_{33}H_{60}O_{16}</td>
<td>C_{33}H_{60}O_{16}</td>
</tr>
<tr>
<td>(M_1)</td>
<td>833.38</td>
<td>835.39</td>
<td>833.38</td>
<td>835.39</td>
<td>835.39</td>
</tr>
<tr>
<td>Cell setting, space group</td>
<td>Monoclinic, (I2)</td>
<td>Monoclinic, (I2)</td>
<td>Monoclinic, (I2)</td>
<td>Monoclinic, (I2)</td>
<td>Monoclinic, (C2/c)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
<td>250</td>
<td>298</td>
<td>297</td>
<td>297</td>
</tr>
<tr>
<td>(a, b, c) (Å)</td>
<td>22.715 (5), 5.656 (2), 85.110 (4)</td>
<td>22.525 (3), 5.634 (1), 85.263 (4)</td>
<td>22.988 (14), 5.641 (5), 86.265 (7)</td>
<td>22.751 (10), 5.650 (5), 86.746 (5)</td>
<td>22.651 (6), 5.653 (3), 89.462 (4)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>90.20 (1)</td>
<td>90.80 (3)</td>
<td>93.52 (12)</td>
<td>93.968 (11)</td>
<td>90.01 (6)</td>
</tr>
<tr>
<td>(V) (Å³)</td>
<td>10934.0 (6)</td>
<td>10688.6 (6)</td>
<td>11164.5 (11)</td>
<td>11123.2 (12)</td>
<td>11455.5 (8)</td>
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<tr>
<td>(D_s) (Mg m⁻³)</td>
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<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Radiation type</td>
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<td>Cu K(\alpha)</td>
<td>Cu K(\alpha)</td>
<td>Cu K(\alpha)</td>
<td>Cu K(\alpha)</td>
</tr>
<tr>
<td>Specimen form, colour</td>
<td>Solid fat, white</td>
<td>Solid fat, white</td>
<td>Solid fat, white</td>
<td>Solid fat, white</td>
<td>Solid fat, white</td>
</tr>
<tr>
<td>Specimen size (mm)</td>
<td>12 \times 1 \times 1</td>
<td>4 \times 1.5 \times 1.5</td>
<td>12 \times 0.7 \times 0.7</td>
<td>12 \times 0.7 \times 0.7</td>
<td>12 \times 0.7 \times 0.7</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Xpert-Pro</td>
<td>BM01b ESRF</td>
<td>Xpert-Pro</td>
<td>Xpert-Pro</td>
<td>Xpert-Pro</td>
</tr>
<tr>
<td>(2\theta) (°) range</td>
<td>0.8–40</td>
<td>0.14–35.5</td>
<td>0.8–45</td>
<td>0.8–45</td>
<td>0.8–45</td>
</tr>
<tr>
<td>(R_f) factors and</td>
<td>(R_p = 0.061, R_{exp} = 0.086)</td>
<td>(R_p = 0.059, R_{exp} = 0.070)</td>
<td>(R_p = 0.064, R_{exp} = 0.095)</td>
<td>(R_p = 0.060, R_{exp} = 0.090)</td>
<td>(R_p = 0.069, R_{exp} = 0.106)</td>
</tr>
<tr>
<td>(\text{goodness-of-fit})</td>
<td>(R_{exp} = 0.019, S = 4.49)</td>
<td>(R_{exp} = 0.022, S = 3.35)</td>
<td>(R_{exp} = 0.041, S = 3.40)</td>
<td>(R_{exp} = 0.034, S = 2.78)</td>
<td>(R_{exp} = 0.037, S = 3.09)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>1.54099</td>
<td>0.79948</td>
<td>1.54099</td>
<td>1.54099</td>
<td>1.54099</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>986</td>
<td>1005</td>
<td>985</td>
<td>996</td>
<td>540</td>
</tr>
</tbody>
</table>

![Figure 2](image2.png)
\(\beta_1\)-2 diffraction patterns of PEP, PSP, PPE, PPS and PSS with PSP rescaled to Cu K\(\alpha_1\).

![Figure 3](image3.png)
Fingerprint area of the \(\beta_1\)-2 diffraction patterns of PEP, PSP, PPE, PPS and PSS with PSP rescaled to Cu K\(\alpha_1\). Peaks are marked with Miller indices. From the (31\ell) reflections (between 20 and 23°) only \(\ell\) is given.
plane. Only with conformations [2–1] and [2–3] for $\beta_1$-2 PPE were plausible structural models found. The slightly lower $R_p$ value of the final [2–3] PPE model suggests this to be the more probable solution. The saturated analogue PPS showed the same conformational preference: the [2–1] model had a bumping problem and a void at the methyl end-plane. Therefore, the choice for the [2–3] PPS model was obvious and in line with the findings for PPE.

3.1.2. $\beta_2$-2 PSS. Unlike the $\beta$ patterns of PEP, PSP, PPE and PPS discussed above, in the case of $\beta_2$-2 PSS the reflections (31ℓ) for ℓ = odd were observed, thus excluding the space group $I2$ as a potential solution. Although, eventually, in the space group $C2/c$ a structural model was obtained, its correctness was questioned because of the monoclinic $\beta$ angle that is close to 90°. After testing orthorhombic space groups with an eightfold general position, possible models were obtained only in $C22_1$ and $Pbna$. The latter was dismissed because of a 270 Å void at the methyl end-plane. The $C22_1$ model refined to a final $R$ value that is 1% higher than that of the $C2/c$ model. Therefore, the latter is taken as the more probable structure solution.

### 3.2. The role of temperature in interpretation of XRPD patterns

In Table 3 the long spacings and strong fingerprint lines of the currently known polymorphs of PEP, PSP, PPE and PPS are listed together with the temperature $T_{\text{datacoll}}$ (in K) at which the data have been collected. Anisotropic thermal expansion properties predominantly influence the position of the strong fingerprint line with the smallest $d$ value ($\beta_2$-2 $0\overline{2}$ PSS) the reflections $\beta_2$-2 PPS discussed above, in the case of $\beta_2$-2 PSS the reflections $\beta_2$-2 PPE (44 Å), $\beta_2$-2 PPE (44 Å) and $\alpha$ PPE (48 Å), but even up to 3–4 Å for $\alpha$ PEP (48 Å), $\beta_2$-2 PPE (47 Å) and $\beta_2$-2 PPE (46 Å). The larger long spacings of Elisabetta and co-workers may be explained by the larger axial divergence, by sample displacement error (because in the reflection geometry they used the positioning of the sample is very critical for accurate low-angle positions), and a lower resolution that may have hidden the presence of a shoulder of the latter. In the fingerprint area it is difficult to discern a broad $\alpha$ peak in the presence of $\beta_2$-2 peaks that are also broad.

<table>
<thead>
<tr>
<th>TAG</th>
<th>$\alpha$</th>
<th>$T_{\text{exp}}$</th>
<th>$\beta_1$-2</th>
<th>$T_{\text{exp}}$</th>
<th>$\beta_2$-2</th>
<th>$T_{\text{exp}}$</th>
<th>$\beta_2$-2</th>
<th>$T_{\text{exp}}$</th>
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<th>$T_{\text{exp}}$</th>
<th>$\beta_2$-2</th>
<th>$T_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEP</td>
<td>43.3 (vs)</td>
<td>296</td>
<td>43.1 (vs)</td>
<td>296</td>
<td>42.4 (vs)</td>
<td>324</td>
<td>–</td>
<td>43.3 (vs)</td>
<td>296</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>4.14 (m)</td>
<td></td>
<td>4.32 (m)</td>
<td></td>
<td>4.34 (m)</td>
<td></td>
<td></td>
<td></td>
<td>4.59 (s)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>4.17 (s)</td>
<td></td>
<td>4.19 (s)</td>
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<td>4.55 (ms)</td>
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<td>4.02 (w)</td>
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<td></td>
<td>4.45 (w)</td>
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<td>n.d. (w)</td>
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<td>3.84 (m)</td>
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<td>4.0 (w)</td>
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<tr>
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<td>295</td>
<td>43.4 (vs)</td>
<td>316</td>
<td>42.8 (vs)</td>
<td>298</td>
<td>–</td>
<td>41.4 (vs)</td>
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<td></td>
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<tr>
<td></td>
<td>4.12 (m)</td>
<td></td>
<td>4.30 (ms)</td>
<td></td>
<td>4.32 (ms)</td>
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<td></td>
<td></td>
<td>4.59 (s)</td>
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**Table 3**

$d$ values of long spacings and strong fingerprint lines (both in Å) of polymorphs of PEP, PSP, PPE, PPS and PSS. X-ray data collected at $T_{\text{exp}}$ (K).
The $\beta$-2 long spacings of PSP, PPE and PPS are smaller than those of the $\beta_1$-2 polymorphs, while for PEP and PSS they are longer. It might be that this explains the relatively high $T_{\text{datacoll}}$ of $\beta_1$-2 PEP and $\beta_1$-2 PSS.

The (600) is the highest-angle strong-intensity reflection in most of the $\beta_1$ patterns, but its position has been shifted remarkably in $\beta_1$-2 PEP (Fig. 3). This shift is attributed to the considerably lower $T_{\text{datacoll}}$ (250 K) of PSP, compared with the 297 K of the other samples, and this led to an anisotropic shrinkage of the unit-cell parameters that mainly affected the middle-sized unit-cell axis.

3.3. Phase transitions and stability of polymorphs

The $T_m$ and phase-transition temperatures obtained with the constant heating-rate experiments (Table 1) show that the symmetric PEP and PSP are $\beta$ stable. The asymmetric PPE, PPS and PSS are $\beta$ stable, although the difference in $T_m$ between the highest melting $\beta$ form and the $\beta$ form is very small for PSS and PPE. The similar melting points explain why a $\beta_1$-2 to $\beta_1$-2 conversion was not observed for PSS and PPE within a week of annealing $\beta_1$-2 PPE below its melting point. For PPS the conversion did occur and was completed in 1 d.

With respect to the reproducibility of the $\beta$ melting points of mono-acid TAGs determined with DTA, Lutton & Fehl (1970) reported that ‘under the best conditions’ an error of $\pm$1 K can be achieved, although stabilization and sample preparation also affect the melting points. Variations in $T_m$’s up to 3 K have been attributed to these phenomena (Lutton et al., 1948). The melting and phase-transition points listed in Table 1 are expected to have an uncertainty of the same order. An optimal stabilization was not feasible for many of the metastable polymorphs because of potential phase transitions.

The heating rate used must be regarded as a parameter that influences the observed temperatures. For example, Elisabetti et al. (1998) obtained for PEP with DSC (heating 5 K min$^{-1}$) a much higher $\beta_1$-2 to $\beta_1$-2 transition temperature (320 K) than the 303 K obtained with our XRPD at 0.5 K min$^{-1}$. The notion that even a modest heating rate may lead to a significant overshoot of the phase-transition temperature implies that one should be careful with conclusions about melting or phase-transition temperatures that have not been measured under the same experimental conditions.

3.3.1. The $\alpha \rightarrow \beta_1$ phase transition. The $\alpha \rightarrow \beta_1$ transition is difficult to analyze with time-resolved XRPD because of the overlap at low angles and in the fingerprint area. With DSC (0.5 K min$^{-1}$) the symmetric TAGs (PSP and PEP) show no significant melting peak before the $\alpha \rightarrow \beta_1$ transition. However, in the case of the asymmetric TAGs (PPE, PPS and PSS) the formation of $\beta_1$ is clearly preceded by the melting of the $\alpha$ phase (DSC data not shown). This is in line with the results of Elisabetti et al. (1998) who concluded from 5 K min$^{-1}$ DSC traces that in PEP the $\alpha \rightarrow \beta_1$ transition is a solid-state transition (no melting peak), whereas in PPE a melt is involved. Apparently, for asymmetric TAGs the $\alpha \rightarrow \beta_1$ transition is more complicated than for symmetric TAGs, suggesting larger conformational changes in the former.

3.3.2. The $\beta_1 \rightarrow \beta_2$ phase transition. In Fig. 4 a selection of diffraction patterns shows the melt and crystallization experiment of PSS. The determined melt and phase-transition temperatures, including the $\beta_2$-2 to $\beta_1$-2 transition point, are marked at the right-hand side of the patterns. The virtually equal positions of the $\beta_2$-2 and $\beta_1$-2 fingerprint maxima, within the accuracy and resolution of the data, and the growth of sharper $\beta_1$-2 peaks at the centres of the broad(er) $\beta_2$-2 diffraction maxima suggests that the $\beta_2$-2 is just a higher-crystalline form of the $\beta_1$-2 polymorph. The close structural relation between the $\beta_1$-2 and $\beta_1$-2 polymorphs, also suggested by Kellens et al. (1990), and the relatively small amount of energy involved in such a transition may explain the difficulty in locating it in the DSC trace. The systematically lower intensity of the (600) reflection in the $\beta_2$-2 patterns compared

![Figure 4](image1.png)

**Figure 4**
Melting and recrystallization of PSS polymorphs: from bottom to top: the starting polymorph $\beta_2$ melts, and after quenching (−30 K min$^{-1}$) and subsequent heating (0.5 K min$^{-1}$) $\alpha$, $\beta_1$ and $\beta_2$ appear and melt. Relevant temperatures are listed to the right of the graph.

![Figure 5](image2.png)

**Figure 5**
Fingerprint area of the polymorphs of PSS.
with \( \beta'_{1-2} \) (Fig. 5) may be an indication of a type of disorder in the direction of the \( a \) axis in \( \beta'_{1-2} \) polymorphs.

The stability of \( \beta'_{1-2} \) differs drastically between TAG groups and also depends on the thermal treatment. When slowly heating (0.5 K min\(^{-1}\)), the transition of the least stable \( \beta'_{1-2} \) to the \( \beta'_{1-2} \) starts 2 K (4 min) after the former’s appearance (Table 1, PSP and PPS). For PSS and PPE this interval is 7 K and for PEP 11 K. This suggests that an exchange of S by E considerably delays the appearance of \( \beta'_{1-2} \) and thus stabilizes the \( \beta'_{1-2} \) polymorph. While the existence of the \( \beta'_{1-2} \) polymorph is difficult to prove for a mono-acid trisaturated TAG (versus different for symmetric TAGs), the transition point and the melting point of the \( \beta'_{1-2} \) polymorph is equal within the accuracy of the temperature measurement and suggest an equal stability. A time- and temperature-resolved diffraction experiment has been carried out with a third PSS capillary sample, taken from the same batch and prepared in the same way as the other two. Unlike the other two samples, this third sample contained \( \beta'_{0} \), but also a small amount of \( \beta'_{2} \). Upon heating this sample at 0.5 K min\(^{-1}\) the diffraction patterns show that the \( \beta'_{0} \) melts 1.5–2 K before \( \beta'_{2} \), so it is concluded that PSS is not \( \beta'_{0}-2 \) but \( \beta'_{2} \) stable.

Questions concerning the precise conditions under which the \( \beta'_{0}-2 \) and \( \beta'_{2} \) crystallize, and whether a tempering process may stimulate this, remain as yet unanswered. Repeated partial melting of \( \beta'_{1-2} \) PSS at 336 K and followed by cooling to 335 K sharpened the \( \beta'_{1-2} \) peaks in the XRPD pattern, but did not induce a conversion to \( \beta'_{0}-2 \), or to \( \beta'_{2} \). After 3 months storage of \( \beta'_{1-2} \) at 330 K a small amount of \( \beta'_{0}-2 \) was detectable. These experiments demonstrate the influence of sample history on \( T_{m} \) values and show that one should take care in drawing conclusions from experimentally obtained thermal data, even if the samples originate from the same batch.

Figure 6
Pair of PSS molecules with facing seats.

Figure 7
Packing of \( \beta'_{1-2} \) PEP. (a) view parallel to the \( b \) axis, (b) view parallel to [130].
3.4. Packing and methyl end-plane

3.4.1. \( \beta'_0 \)-2 PEP, \( \beta'_1 \)-2 PSP, \( \beta'_1 \)-2 PPE and \( \beta'_1 \)-2 PPS. In all the \( \beta'_1 \)-2 structures discussed in this publication the conformation of the chair-shaped molecules shows the typical \( \beta' \) bend of \( \sim 130^\circ \) between the back and back leg of the chair (the same as in van Langevelde et al., 2000; Sato et al., 2001). Also, in all the \( \beta' \) structures the molecules are packed with seats facing each other, but being slightly tilted, while the back of one molecule is adjacent to the front leg of the other one (Fig. 6). The legs of one (upper) molecule (Fig. 6, left-hand side) are packed in the same layer as the back of the other (lower) molecule, but the legs of the lower molecule and the back leg of the lower molecule (Fig. 6, right-hand side) are packed in another, different layer than its front leg and the back of the upper molecule. The pairs of molecules form ‘two-pack’ layers with a double-chain length thickness. The unit cell of the \( \beta'_1 \)-2 structure contains two such ‘two-packs’ that are related to each other by a \((1\overline{1}0)\) translation. The bends in the molecules point in the same direction, as a result of which the ‘two-packs’ approach each other at the methyl end-plane with the same angle as the bend in the molecules (Fig. 7). The methyl end-groups at one side of the interface between the ‘two-packs’ point in between two methyl end-groups of the adjacent ‘two-pack’ (Fig. 7b). The view along the \( b \) axis shows a difference between the packing of the symmetric and asymmetric \( \beta'_1 \)-2 structures: In the symmetric structures the chains at the methyl end-plane are aligned projected along the \( ac \) plane (Fig. 7a), whereas in the asymmetric structures the chain ends of one ‘two-pack’ point between two other chains of the neighbouring ‘two-pack’ (Fig. 8).

The precise location of the seat of the chair-shaped molecules between the dominating columns of electron density of the zigzag chains is a point that deserves extra attention. If opposing chair seats at the front-leg side bump, the seat position is likely to be incorrect. The solution to this bumping problem is similar to that described for \( \beta \)-2 structures: rotation of the seat plus front leg along the back-leg axis until the front leg coincides with a neighbouring column of electron density (van Mechelen et al., 2006b).

However, at the given resolution of the data two serious ambiguities exist in the packing of the \( \beta' \) structures of PPS, PPE, PSP and PEP. The first is the position of the methyl end-plane. When the molecules are shifted by \( c/4 \) and rotated by \( 180^\circ \) along the direction of the \( c \) axis, a packing can be realised that fills the columns of electron density of the parallel parts of the acyl chains, but with the methyl end-plane and the glycerol zone interchanged and having the seat at a different position. The \( R \) values for both packings are virtually the same so from the XRPD data no choice can be made for the methyl end-plane position. This ambiguity may be solved by comparing with the single-crystal data of \( \beta'_1 \) CLC. At room temperature this crystal structure is orthorhombic, but at lower temperatures \( \beta'_1 \) CLC becomes monoclinic. Since this orthorhombic to monoclinic transition is reversible, it is likely that no changes are involved other than small shifts and rotations. The similarity between the powder pattern of the monoclinic \( \beta'_1 \) CLC and the \( \beta'_1 \) patterns of the present study supports a structural equivalence and for this reason the methyl end-plane position has been taken as conforming to that in \( \beta'_1 \) CLC (van Langevelde et al., 1999).

The second ambiguity is the orientation of the second molecule in the asymmetric unit of the \( I2 \) structure. Each molecule forms a seat-facing pair with a symmetry copy of itself. When the lower-left quarter of the unit cell (Fig. 7a) is filled by a molecule pair of molecule (1), the upper-left quarter is filled by molecule (2). When molecule (1) has approximately the proper configuration, molecule (2) may be obtained in two ways: by shifting a copy of molecule (1) by \( a/2 \) relative to molecule (1) (option 1), or by shifting a copy of molecule (1) by \( a/2 \) plus an additional \( 180^\circ \) rotation with respect to an axis at \( (3a/4, c/4) \) perpendicular to the \( ac \) plane (option 2). After optimization by FOX, both molecule combinations lead to structure solutions that differ mainly in the position of the seat of the second molecule. Just as with the previous ambiguity, the single-crystal data of \( \beta'_1 \) CLC has been used to select the second option. The seat-position ambiguity is not unique for structure solution of TAGs from powder diffraction data. Even in the single-crystal structure solution of \( \beta'_1 \) CLC, the seat position was a problem (private communication) and only from a \( 2mF_0 - DF_{\text{calc}} \) electron-density map could it be established unambiguously (van Langevelde et al., 2000).

3.4.2. \( \beta''_0 \) PSS. The unit cell of the \( \beta''_0 \)-2 structure of PSS also contains two ‘two packs’, but these are related by an inversion centre. This makes the bends in the two ‘two-packs’ point in opposite directions, whereas the chains of the approaching ‘two-packs’ at the methyl end-plane are not inclined but parallel and aligned (Fig. 9). The methyl end-plane of the ‘two-packs’ is stepped (Fig. 9a) and can be denoted as a \((2-2)\) interface as the \( sn \)-2 chains of neighbouring ‘two-packs’ are in line, analogous to the \( \beta''_0 \) polymorphs of these TAGs (van Mechelen et al., 2008).

3.5. Comparison of \( \beta'' \) structures

The fingerprint area of the diffraction patterns of all the \( \beta'' \)-2 structures is dominated by the
(600) and (31\ell) reflections (Fig. 3). The lattice planes (600), (318) and (318) are related to the most intense fingerprint diffraction maxima because of their orientation relative to the chain packing (Fig. 10). Based on FT-IR measurements on microcrystals, Yano et al. (1997) suggested an O\_1 subcell for the \( \beta'_{1-2} \) structure. This subcell is found in the single-crystal structure of the \( \beta'_{1-2} \) CLC structure (van Langevelde et al., 2000) and does not conflict with the data of the \( \beta'_{1-2} \) structures of this paper. However, at the resolution to which the \( \beta'_{1-2} \) TAGs diffract (not beyond 3 Å), the orientation of the zigzag planes of the acyl chains, and thus the subcell, cannot be established unambiguously. Since the same problem applies to \( \beta''_{6-2} \), it is obvious that the usefulness of the subcell is quite limited.

The ‘two-packs’ in the \( \beta' \) structures can be described as two stacked dimers that each consist of two symmetry-related molecules. The dimeric symmetry (\( 2_1 \) axis parallel to the \( b \) axis) is the same in all cases, but the stacking of the dimers can be different. In the \( \beta'_{1-2} \) structures of this work the dimers in the ‘two-packs’ are not symmetry related. In the orthorhombic \( \beta'_{1-2} \) (room-temperature) crystal structure of CLC (van Langevelde et al., 2000) they are symmetry-related by a \( a \) glide perpendicular to the \( a \) axis and in the \( \beta''_{6-2} \) of PSS the dimers are related by a \( (1\frac{1}{2} \) \( 0) \) translation.

The symmetric and asymmetric \( \beta'_{1-2} \) TAGs appear to have different conformations, the former a [1–2] and the latter [2–3]. This difference in conformation suggests a relation to their different behaviour at the \( a \to \beta' \) transition. For the symmetrical group that does not exhibit a clear \( a \) melting it seems likely that the [1–2] \( \beta' \) conformation is maintained from the \( \beta'' \) form. However, the asymmetric TAGs do show \( a \) melting and this may be related to the change from the [1–2] conformation to the [2–3] conformation.

Judging from the \( \beta'_{1-2} \) models and the \( \beta''_{6-2} \) PSS model, the transition of \( \beta'_{1-2} \) PSS to \( \beta''_{6-2} \) PSS has to involve an inversion of the orientation of every other ‘two-pack’. This symmetry relation between the ‘two-packs’ in \( \beta'_{1-2} \) versus \( \beta''_{6-2} \) is similar to that found for the ‘three-packs’ in the \( \beta_{2-3} \) versus \( \beta_{1-3} \) polymorphs of cis-mono-unsaturated TAGs: in the lower-melting polymorph the ‘three-packs’ are related via the translation \( (1\frac{1}{2} \) \( 0) \), while in the higher-melting one they are related by a centre of symmetry (van Mechelen et al., 2006b).

It should be noted that apart from the \( \beta'_{1-2}, \beta''_{6-2} \) and \( \beta'_{1-2} \) discussed in the present paper, other types of \( \beta' \) structures do exist. For example, the crystal structure of a \( \beta'_{-2} \) polymorph of PPM has been solved from single-crystal data (Sato et al., 2001). This asymmetric \( \beta'_{-2} \) structure has two molecules in the asymmetric unit, just like the \( f2 \) structures of the present paper, but the two molecules have different conformations, [2–1] and [2–3], that together form a seat-facing pair. A (calculated) powder diffraction pattern clearly shows that this compound belongs to a different class of \( \beta' \) structures because the reflection (600) is missing. It seems relevant to note that the \( \beta'_{-2} \) PPM single crystal was crystallized from \( n \)-hexane, whilst the \( \beta' \) polycrystalline material used for the present work was obtained without solvent.

3.6. Comparison of \( \beta' \) and the \( \beta \) structures

The \( \beta' \)-polymorphs presented in this paper are either in a [1–2] conformation (PEP, PSP, PSS) or in a [2–3] conformation (PPE, PPS), and have a bend between the back and the back leg. It was noted that in all cases the seat of the chair is a C18 chain (E or S), apparently a conformation that is energetically favourable, and this may explain why the [2–3] conformation of PPE and PPS both have a shorter sn-2 chain.

![Figure 9](image)

**Figure 9**

Packing of \( \beta''_{6-2} \) PSS: (a) view parallel to the \( b \) axis; (b) view parallel to [310].

![Figure 10](image)

**Figure 10**

View parallel to the chain direction of half a \( \beta'_{1-2} \) PSP ‘two-pack’. Dotted lines mark the orientation of the lattice planes corresponding to the main fingerprint lines. Solid lines: the \( O_1 \) subcell in line with that present in \( \beta'_{1-2} \) CLC.
In contrast, the $\beta\prime-2$ polymorphs of all these materials (see paper III of this series; van Mechelen et al., 2008) are all in a $[1\bar{3}0]$ conformation. In this conformation the back and the back-leg of the seat, formed by the $sn\!-\!1$ and $sn\!-\!2$ chains, are lined up and the parallel planes of the zigzag chains form a triclinic subcell. The different molecular conformations in $\beta\prime-2$ versus $\beta-2$ imply that rather complicated changes are required in the transition from $\beta\prime-2$ to $\beta-2$ and this may explain the difficulty in obtaining a $\beta$ phase. The symmetric PEP and PSP are $\beta$ stable and since the $\beta-2$ of PSP and PEP melt at lower temperatures, a $\beta$ to $\beta$ conversion cannot be observed. It seems likely that this $\beta$ phase can be obtained only if the melt-mediated $\beta\prime-2$ can be avoided, e.g. by crystallization from a solvent (Lutton & Hugenberg, 1960). The latter authors reported that $\beta-2$ PSP transforms into $\beta\prime\prime-2$ at 338 K via the melt. The melting indicates a change in conformation and/or packing, in line with the structural differences determined. The asymmetric PPS and PSS, and probably also PPE, are $\beta-2$ stable, as shown from the melting points. The $\beta\prime-2$ to $\beta-2$ conversion rate in these cases is very slow, if conversion occurs at all, so measuring the conversion with DSC is impossible. With temperature-resolved XRPD the precise conditions to stimulate the transition in a controlled and reproducible way have not been established yet.

4. Conclusions

The $\beta\prime\prime-2$ structures of PSP, PEP, PPS and PPE have been solved from high-resolution powder diffraction data in the space group $I2$. The packing is in line with the orthorhombic single-crystal structure of $\beta\prime\prime-2$ CLC (van Langevelde et al., 2000). The presence of two molecules in the asymmetric unit complicated the structure solution and, together with dominant zone problems and peak overlap in the diffraction pattern, it hindered the determination of the orientation of the zigzag planes of the acyl chains. Unlike the $\beta-2$ structures of these compounds (van Mechelen et al., 2008) the symmetric and asymmetric $\beta\prime\prime-2$ structures have different molecular conformations. The structure of a novel $\beta$ polymorph of PSS, named $\beta\prime\prime\prime\prime-2$, was solved in the space group $C2/c$. The molecule has a characteristic $\beta$ bend conformation. Time- and temperature-dependent XRPD experiments showed that both $\beta\prime\prime-2$ PSS and $\beta\prime\prime\prime\prime-2$ PSS melt at lower temperatures than the $\beta$ polymorph, so justify the conclusion that PSS is $\beta$ stable. The difference in molecular conformation between the $\beta\prime\prime-2$ polymorphs and the $\beta-2$ polymorph makes a $\beta-2$ to $\beta\prime-2$ solid-state transition unlikely. For the $\beta\prime\prime-2$ structures as well as $\beta\prime\prime\prime\prime-2$, the dominant zones in the fingerprint area of the X-ray pattern can be correlated with the layered packing of the acyl chains.

In the case of the structure determination of cis-mono-unsaturated $\beta-3$ type TAGs it was shown that the diffraction data are not very sensitive to rotational freedom of zigzag chains around their long axis (van Mechelen et al., 2006a). This also holds for the $\beta\prime\prime-2$ structure of PSS in $C2/c$. This structure has a single molecule in the asymmetric unit just like the $\beta-3$ structures. The rotational freedom is an even more serious problem in the $\beta\prime\prime\prime\prime-2$ structures because they have two molecules in the asymmetric unit, while their powder patterns do not have more independent reflections. Thus, no firm conclusions are possible about the orientation of the planes of the zigzag chains on the basis of non-atomic resolution XRPD data alone.

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