## Supporting Information — Molecular order in cold drawn, strain-recrystallized Poly-ε-caprolactone

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#### Uncertainties of pole distribution functions

The uncertainty of the pole distributions results from the determination of the integrated area (fig. 4), being in the range of 5 %, and the normalization (denominator in eq. 2), which involves the extrapolation of the integrated area to  $\beta = 90^{\circ}$ . This extrapolation can be done unambiguously for the perpendicular orientation, but is error-prone for a parallel orientation of the stretching direction and tilting axis (inset of fig. 4).

### Crystallization and assignments

To identify vibrational absorption bands originating from TMs being solely related to crystalline sub-chains, the following experiment is performed: First a semi-crystalline sample is heated from 303 K to 343 K and FTIR-spectra<sup>1</sup> are recorded at temperature steps of 1 K. As soon as the crystallites melt, obvious changes appear in the spectra resulting from the vanishing crystalline symmetry (fig. 1a–d).<sup>1</sup> From these and further FTIR-experiments<sup>2</sup> the spectral positions (vibrational frequency:  $\bar{\nu}_c$ ) and band-widths ( $w_{\rm FWHM}$ ) of vibrational absorption bands originating from crystalline or amorphous units are determined (tab. 1) in manuscript). These measurements build the foundation of the band-decomposition by fitting sums of pseudo-Voigt-profiles to the spectra (fig. 1a–d & fig. 3 in the manuscript). Furthermore, Density Functional Theory (DFT) calculations are performed employing the B3LYP theory and 6-311++G(2d,2p) basis functions to assign the vibrational bands to certain TMs.<sup>2–5</sup> The resulting assignments can be found in tab. 1 in the manuscript and the TMs are shown in fig. 2. Several bands related to COC stretching modes of the main chain (MC) are discussed in this work. One at  $(1295 \pm 0.2)$  cm<sup>-1</sup>, with a TM parallel to the crystallites'  $\underline{c}$ -axes, and a group of vibrations between 920 cm<sup>-1</sup> and 990 cm<sup>-1</sup> exhibiting different orientations with respect to the MC (cf. tab. 1 and fig. 1a, b). The analysis of the bands  $\nu'_{1a}(COC)$ ,  $\nu'_{1c}(COC)$  and  $\nu''_{1a}(COC)$ , respectively at 933, 961 and 973 cm<sup>-1</sup>, is hampered by some underlying broad or diffuse amorphous bands, which change upon crystallization. This becomes obvious by a tilt of the baseline of these three peaks during the kinetic experiment (fig. 1c, and fig. 3a & tab. 1 in the manuscript). Consequently, the deduced order parameters may deviate from the real ones, as the the baseline can not be corrected perfectly. The influence on  $\nu_{1c}(COC)$  is much weaker, as this band shows less overlap with the neighbouring, and can be baseline-corrected and fitted consistently in the amorphous and crystalline state.

 $<sup>^{1}</sup>$ IR-spectra are recorded with a Bio-Rad-FTS-6000 spectrometer and a resolution of 2 cm<sup>-1</sup> using the connected Bio-Rad-UMA-500 IR-microscope and a Linkam THMS 350 heating stage.

<sup>&</sup>lt;sup>2</sup>IR-spectra are obtained upon quenching molten samples down to a certain crystallization temperature,  $T_x = 296$  K.

In the kinetic experiments its integrated absorbance, therefore perfectly agrees with the one of the other bands assigned to the crystalline state (fig. 1f). For poly(ethylene-glycol) the discussed region around 960 cm<sup>-1</sup> is supposed to bear conformational sensitivity.<sup>6–8</sup> Whether this applies to PCL as well is not clear, as bands of crystalline strands (which have a fixed conformation) appear upon crystallization and mask effects on the amorphous phase.

The C=O stretching bands,  $\nu$ (C=O), have been assigned and discussed in the literature before, as carbonyl groups appear in various organic and inorganic substances (tab. 1).<sup>9–15</sup> Slightly different orientations of the the underlying TM with respect to the MC have been reported, but the implications for the molecular order parameter tensor (S) are minor.<sup>9,11</sup> Consequently, all calculations are based upon a model, where the C=O-bond is perpendicular to the MC and well aligned with the TM of its stretching vibration.

The dicussed C=O stretching band is so strong, that the imaginary part of the refractive index (n'') reaches a value of about -0.6. Consequently, the real part (n') shows a significant dispersion within the spectral range of the absorption band: In the low frequency part of the band (around the inflection point) n' is increased by up to 0.3, whereas for higher wavenumbers n' is reduced by about the same value.<sup>16,17</sup> This complicates the application of IR-TMOA, as (1) due to reflections and dispersion the band shapes of the two bands are altered, and (2) the propagation direction varies depending on the wavenumber; both in a non-negligible fashion. Consequently, beam propagation and the absorption coefficient cannot be separated.<sup>16,18</sup> Therefore, transmission (or equivalently absorbance) and beam propagation are calculated for every wavenumber polarization ( $\phi$ ) and inclination ( $\beta$ ) simultaneously.

The CH<sub>2</sub>-stretching band of crystalline polymer strands,  $\nu_c$  at  $\approx 2894$  cm<sup>-1</sup>, is assigned based on the kinetic measurements described above (tab. 1 in the manuscript). In the molten state (T > 333 K), this band is absent (fig. 3 in the manuscript). The variations in this region (2880–2900 cm<sup>-1</sup>) are due to interference.<sup>19</sup> As soon as the sample crystallizes, the peak either grows in between the already existing CH<sub>2</sub> stretching bands, or adds some extra absorbance to a peak of amorphous origin. In any case the peak can be approximated as an additional contribution to the absorbance pattern. The corresponding TM is reported to be exactly perpendicular to the MC, and therefore, also to the crystalline  $\underline{c}$ -axis.<sup>9,20</sup> The effect of the surrounding absorption bands (as shown in fig. 3d of the manuscript) on the refractive index at 2894 cm<sup>-1</sup> is accounted for by modelling the full complex refractive index based on the absorbance spectrum and a Kramers-Kronig transformation.<sup>21</sup>

### **IR-TMOA** and **XRD** pole figures

Two fundamentally different methods, X-ray Diffraction and IR-spectroscopy, are utilized in this work to quantify order. The former senses the number of of crystal lattice planes in a certain direction, *i.e.* their orientation distribution. The latter is a moiety-specific technique sensing vibrational Transition Moments (TMs) of specific molecular groups (tab. 1 & fig. 2 in the manuscript).

The area of IR absorption bands (integrated absorbance  $A_{int}$ ) is related to the component of its vibrational TM vector,  $\underline{v}$  (*cf.* fig. 2 in the manuscript), along the electric field,  $\underline{E}$ :  $A_{int} \propto \langle (\underline{v} \cdot \underline{E})^2 \rangle$ .<sup>22</sup>  $\langle \ldots \rangle$  denotes the average over the whole illuminated area.  $\underline{E}$  can be varied in all spatial directions (fig. 3 in the manuscript). Therefore, the analysis of  $A_{int}$ allows to determine the three-dimensional (3D) order parameter tensor: S, an analogue of Herman's orientation function, which describes the quadratic average of the number of TMs or any other vectorial quantity oriented in the full 3D-space ( $\underline{i}, \underline{j} \in [\underline{\hat{x}}, \underline{\hat{y}}, \underline{\hat{z}}]$ ).<sup>16,22,23</sup>

$$\boldsymbol{S}_{ij} = \frac{1}{C} \left( \frac{3}{2} \left\langle (\underline{v} \cdot \underline{i}) (\underline{v} \cdot \underline{j}) \right\rangle - \frac{1}{2} \right)$$
(1a)

$$C = \sum_{i=x,y,z} \left\langle (\underline{v} \cdot \underline{i})^2 \right\rangle \tag{1b}$$

If S is a diagonal matrix, the principal axes of the orientation distribution agree with the coordinate system (but not necessarily the crystal axes themselves). The diagonal elements

describe the alignment of the vectors  $\underline{v}$  with the coordinate axes: A value of  $S_{xx} = 1$  indicates that all  $\underline{v}$ 's are aligned with  $\hat{\underline{x}}$ ,  $S_{xx} = -1/2$  is obtained if all  $\underline{v}$ 's are perpendicular to  $\hat{\underline{x}}$ . In case there are as many components of vectors along  $\hat{\underline{x}}$  as in the isotropic case, we find  $S_{xx} = 0$ . Please note, that does not imply an isotropic distribution, as *e.g.* one could find preferential alignment along  $\hat{\underline{y}}$  on expense of  $\hat{\underline{z}}$ .<sup>23</sup> If S contains off-diagonal elements, the coordinate system of the sample would be rotated with respect to the principal axes of orientation. But as S is symmetric, it can always be diagonalized. And the eigenvalues of the resulting matrix describe the alignment along the corresponding eigenvectors, just as discussed before for  $\hat{\underline{x}}$ ,  $\hat{\underline{y}}$  and  $\hat{\underline{z}}$ . Rotational symmetry is found when the diagonal representation of S has two identical elements. Then the third non-trivial element of S is the well-known order parameter of Herman. For the sample studied here, IR-TMOA reveals off-diagonal elements of negligible amplitude, and consequently, we limit our discussion to the diagonal elements of S.

The integrated area  $(I_{\rm X})$  of the studied diffraction peaks is proportional to the number of (110) and (200) lattice planes with a normal parallel to the scattering vector  $\Delta \underline{k}$  (fig. 3 in the manuscript).  $\Delta \underline{k}$  is varied once within the  $\hat{\underline{y}} \cdot \hat{\underline{z}}$ -plane (|| in fig. 4a in the manuscript) and once within the  $\hat{\underline{x}} \cdot \hat{\underline{z}}$ -plane ( $\perp$  in fig. 4b in the manuscript). The obtained areas are converted into two two-dimensional pole distribution functions (fig. 6 in the manuscript), that are proportional to the ratio, in eq. 2.<sup>23</sup> The order in the  $\underline{y} \cdot \underline{z}$  plane is given by the two-dimensional, scalar order parameters with respect to  $\underline{z}$ :  $S_{2D,z}^{yz}$ ; and in the  $\underline{x} \cdot \underline{z}$  plane:  $S_{2D,z}^{xz}$ .<sup>23</sup> These are not to be confused with off-diagonal elements of the 3D order parameter tensor.

$$S_{2\mathrm{D},z}^{iz} = \frac{3}{2} \underbrace{\frac{\int_{0^{\circ}}^{90^{\circ}} \mathrm{d}\beta I_{\mathrm{X}} \cos^{2}\beta \sin\beta}{\int_{0^{\circ}}^{90^{\circ}} \mathrm{d}\beta I_{\mathrm{X}} \sin\beta \mathrm{d}\beta}}_{\text{pole distribution function}} -\frac{1}{2}$$
(2)

with  $i \in [x, y]$ ,  $\beta$  representing the tilt angle (fig. 4 in the manuscript). These values are solely based on the number of crystal directions within the  $\underline{\hat{x}} \cdot \underline{\hat{z}}$  or  $\underline{\hat{y}} \cdot \underline{\hat{z}}$  planes and correspond to a hypothetical uniaxial alignment along  $\underline{\hat{z}}$ . Therefore, these parameters would describe usual nematic order parameters for a director along  $\underline{\hat{z}}$ .

A conversion of these two two-dimensional order parameters into the 3D order parameter tensor cannot be performed exactly, as the pole distribution parallel to the sample plane is not known. An approximation can be given based on the assumption that all plane-normals are aligned with one of  $\hat{x}$ ,  $\hat{y}$  or  $\hat{z}$  (tab. 1 in the manuscript). Naturally, this assumption can not be true for the [110]- and [200]-directions simultaneously.

In summary, complementary information is obtained by IR-TMOA and XRD pole figures. The former technique is sensitive to molecular moieties: *crystalline or amorphous*, whereas the latter senses periodic distances, *i.e.* primarily *crystallites*. The intensity of the absorption and diffraction peaks ( $A_{int}$  and  $I_X$ ) varies upon tilting ( $\beta$ ), allowing to quantify the order of different lattice directions: respectively [001], and [110], [200].

# Order parameter tensor from two-dimensional order parameters

In this section, relations between two-dimensional and three-dimensional quantifications of molecular order are established. In particular, we deduce the elements  $(S_{ii})$  of the threedimensional order-parameter tensor  $(\mathbf{S})$  from 2 two-dimensional order parameters  $(S_{2D}^{ij})$ . Here  $S_{2D}^{yz}$  and  $S_{2D}^{xz}$  are obtained from measurements of orientational order respectively in the  $\hat{y} \cdot \hat{z}$ - and  $\hat{x} \cdot \hat{z}$ -plane under the assumption of rotational symmetry with respect to the  $\hat{z}$ -axis. The equations rely on the assumption, that perfectly perpendicular planes are measured, both containing 2 of the principal absorption directions.

First, we determine the mean values of orientation  $(A_i, i \in [x, y, z])$ , quadratically aver-

aged over the full three-dimensional space.

$$A_{z}^{iz} = \frac{2S_{2\mathrm{D}}^{iz} + 1}{3} \qquad \text{for } i \in [x, y] \tag{3}$$

$$A_z = 2 \left[ 1/A_z^{xz} + 1/A_z^{yz} \right]^{-1} \tag{4}$$

$$A_{i} = A_{z} \frac{1 - S_{2D}^{iz}}{2S_{2D}^{iz} + 1} \qquad \text{for } i \in [x, y] \tag{5}$$

This finally leads to the order parameter tensor in a diagonal representation.

$$S_{ii} = \frac{3A_i - 1}{2} \qquad \qquad \text{for } i \in [x, y, z] \tag{6}$$

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Figure 1: a–d) show the temporal evolution of vibrational absorption bands of crystalline structures in PCL after a quench from 343 K down to  $\approx 296$  K. Spectra (solid lines), recorded within  $\approx 2$  s at the times indicated by the filled symbols in e and f, are stacked vertically (first spectrum is at the bottom). For the last spectrum (top) the fit-curves are given by the coloured dashed lines as well as the different contributions to the absorption bands (green lines), and the tangential baseline (black dashed line). e) Variation of temperature with time; f) holds the normalized integrated absorbance of the bands at  $\approx 840$  cm<sup>-1</sup> (blue diamonds, *cf.* a), (1295.2 ± 0.2) cm<sup>-1</sup> (red diamonds, *cf.* b), at  $\approx 3435$  cm<sup>-1</sup> (magenta diamonds, *cf.* d) and at  $\approx 3450$  cm<sup>-1</sup> (magenta circles). Errorbars are in the range of the symbol-size. Note, that only the band at  $\approx 3450$  cm<sup>-1</sup> originates from TMs related to amorphous structures (magenta circles). In c additionally the second derivative (dashed cyan line, indicated  $\Delta^2$ ) of the first spectrum (solid cyan line) is shown.