The thermal behavior of ultrathin, semi-crystalline films of oligo(ε-caprolactone) (OCL) with hydroxy or methacrylate end groups, is studied by the Langmuir technique in dependence on mean molecular areas and crystallization temperatures. The films on solid substrate as obtained by Langmuir–Schaef er transfer exhibit different lamellar thicknesses, crystal number densities, and lateral sizes. The melting temperature of OCL single crystals at the water and solid surface is proportional to the inverse crystal thickness and generally lower than in bulk PCL. An influence of OCL end groups on the melting behavior is observed mainly at the air–solid interface, where methacrylate end capped OCL melts at lower temperatures than hydroxy end capped OCL. Comparing the underlying substrate, melting/recrystallization of OCL ultrathin films is achievable at lower temperatures at the air–water interface than at the air–solid interface, where recrystallization is not identifiable. Recrystallization at the air–water interface generally occurs at higher temperatures than the initial crystallization temperature. The surface pressure, as an additional thermodynamic variable, seems to further affect the crystallization behavior, with crystal thickness and lateral growth rate increasing with surface pressure. The results presented here are important when designing temperature-sensitive or active nanostructured materials or interfaces based on OCL.

1. Introduction

Poly(ε-caprolactone) (PCL) is an important material in biomaterial applications, especially as a thermal switch with a transition close to physiological conditions. PCL oligomers (OCLs) are therefore important building blocks for multifunctional materials owing to biodegradability, while known synthesis pathways into various end group functionalized telechelics enable flexible strategies for creating thermoreversible crystalline regions. The interface to the predominantly aqueous environment is of paramount importance for the performance of OCL based materials in biological systems, since nearly all interactions are mediated upon direct contact. The behavior of polymer chains at the interface is very different from the behavior of chains in the bulk, which are buried and strongly entangled, while the chains at the interface are far less restricted. Due to the interaction with water molecules, the energetic situation of polymer chains at the interface will also differ from their counterparts in bulk. Limiting of chain flexibility by entanglements and crystallites as well as low free volume means that water uptake into bulk PCL is restricted. Yet, water might still interact favorably with the chains and act as a partial solvent. Then, their phase transitions like crystallization, as well as other temperature dependent phenomena such as the glass transition, are strongly affected. This is especially applicable for swellable networks and nanostructured materials, where water uptake is near instantaneous and can therefore affect the whole material, not just its surface. Adequately predicting the switching behavior of OCL-based multifunctional materials in medical applications clearly necessitates taking into account the influence of water, especially at the polymer–water interface.

Thin film experiments are the common approaches to study the behavior of polymer chains at interfaces. These experiments are usually carried out on substrates and in the absence of water and are probably not well suited to replicate the crystallization of chains at the surface of a medical device. On solid surfaces, the polymer chain mobility is extremely constrained, and the solid surface defects cause crystallization by heterogeneous nucleation or prefreezing (formation of thin crystalline layer above melting temperature, $T_m$). The melting temperature of crystalline films on solid surface can be thickness dependent, for example, from PCL 23K film on a graphite surface, a 127 nm film melts at 63 °C while a thinner 13 nm film melts at 84 °C. A recrystallization can typically not be observed due to its occurrence during the heating process or dewetting and irreversible adsorption of melted partially crystalline polymer film on solid surfaces.
Here, we hypothesize that we can understand the influence of water on the thermodynamic transitions of PCL by studying the crystallization and melting of OCL from Langmuir films in dependence of subphase temperature and surface pressure (σ). While one would not expect water to be a good substrate for investigating relatively hydrophobic polymers such as PCL or poly lactide, experiments with polymers in Langmuir films have taught us that these molecules form 2D polymer solutions at the air–water interface, with the chains of some medically relevant (co)polymers adopting extended conformations as in good solvents. The ability of these (co)polymers to form stable investigable films at the air–water interface is due to the hydration of their polar chemical groups, which anchor to the water surface and overall impart an amphiphilic nature to the spread hydrophobic polymer.

Langmuir monolayers are ideally suited for this task, because they avoid the influence of an underlying solid substrate and allow the chains to get swollen by water. During crystallization at the air–liquid interface, the layers have a negligible shear modulus or viscosity, meaning that the effects of chain entanglements on crystallization can be excluded, allowing the study of crystallization without restriction on chain transport, resulting in a crystallization process close to thermodynamic equilibrium.

While polymer crystallization in Langmuir monolayers has been thoroughly investigated, there is an open question, which has so far not been addressed. In bulk and in solution, crystallization is regulated by the degree of undercooling under a characteristic crystallization temperature \( T_c \). In Langmuir monolayers of polymers such as poly(3-R-hydroxybutyrate) or PCL, crystallization depends on the surface pressure as a second thermodynamic state variable, and crystallization is only observed above a critical surface pressure \( \pi^* \). The influence of undercooling on the crystallization from melt or solution in terms of crystallization and nucleation rates as well as lamella thickness is extremely well described. It remains to be seen whether the surface pressure has a similar effect as temperature, so that with increasing “overpressure”, crystals become thinner while nucleation and growth rates increase.

To answer this question, crystals grown under different conditions are transferred to solid substrates and their thickness is measured via atomic force microscopy (AFM), which further allows the construction of Gibbs–Thomson plots for OCL crystals in contact with water. We expect the equilibrium melting temperature \( T_{m,\infty} \), and also the characteristic crystallization temperature \( T_c \), to be substantially lower than in bulk or for crystals at the air–solid interface. The end groups of telechelics, which are used to build architecture materials but have not been converted in a chemical reaction, have different polarity and steric requirements and will probably also affect the crystallization behavior. We expect the transitions in water shifting to lower temperature when end groups are more hydrophilic.

For this study, two different telechelic OCLs having either hydroxy or methacrylate end groups are applied. Hydroxy and methacrylate end capped polymers are valuable for construction of architected materials, where diols are joined via diocyanate linkers and methacylates form networks, both under ambient conditions. OCLs with dimethacrylate or diol end groups are therefore commonly used to introduce thermal switching capability into (multi)functional materials. Yet, these end groups also differ in size and hydrophilicity, and therefore serve as a representation of either small and hydrophilic, or large and hydrophobic chain terminations, which could occur depending on material architecture. In bulk, it was reported that the influence of end group functionalization on \( T_m \) of ethylene glycol initiated OCL diols (OCMDMs) and OCL dimethylacrylates (OCMDMs) was very small when number average molecular weights \( M_n \) were above 4000 g mol\(^{-1}\). Therefore, the applied OCL samples for this study are within a \( M_n \) range of 4000 to 8000 g mol\(^{-1}\) with a polydispersity index of 1.2, where OCL molecules are also known to form laterally large crystals, which are observable by Brewster Angle Microscopy (BAM) at the air–water interface. The OCMDOL and OCMDME used for this study were initiated by either 1,4-butanediol or diethylene glycol. While even for short OCMDOLs with \( M_n \) of about 1200 g mol\(^{-1}\), the effect of the central initiating unit on the crystallization in bulk is negligible, at the air–water interface, an influence cannot be ruled out due to the “anchoring effect” of ethylene glycol.

Crystallization is carried out at air–water interface at constant film area induced by cooling and compressing using the Langmuir trough barriers, resulting in isothermal crystallization with a rate that decreases with time at constant crystallization temperature \( T_c \). In that way, it is possible to observe isolated crystals whereas under constant pressure, films become almost entirely crystalline. Two water subphase temperatures of 12 °C and 21 °C are used as isothermal crystallization temperatures. The melting and recrystallization of OCL films at the air–water interface is studied by altering water subphase temperature at a constant rate. The thermal behavior of partially crystalline OCL films is monitored by in situ Brewster angle microscopy and surface pressure changes. Partially crystallized and recrystallized OCL films from the air–water interface are transferred to silicon substrates via the Langmuir–Schaef er (LS) method (Figure 1) for crystal thickness and morphological investigation by atomic force microscopy. On these samples, using polarizing optical microscopy equipped with a heating stage, the melting temperature at the air–solid interface is studied by heating with a constant rate of 2 °C ± 0.4 °C min\(^{-1}\). The results are analyzed with regard to the Gibbs Thomson equations for crystallization and melting, to facilitate a prediction of the melting temperatures of PCL crystals in aqueous environments. To determine the influence of water, crystallization and melting of OCL at the air–water interface will be compared to results from bulk and from the air–solid interface.

2. Results and Discussion

2.1. OCDOL and OCDME Crystallization at Air–Water Interface at Different MMA and \( T_c \)

In the initial step of OCL film crystallization at the air–water interface, compression of spread molecules yields a typical mean molecular area (MMA) versus surface pressure isotherm (Figure 2a,b). The MMA is the mean surface area occupied per \( \varepsilon \)-caprolactone repeat unit, calculated from the number of spread repeat units and the total area of the film. In the OCL surface pressure versus area isotherms, a sudden decrease in surface pressure at MMA <30 Å\(^2\) is accompanied with the
formation of observable crystals in the Brewster Angle microscope. This critical surface pressure $\pi^c$ in the OCDOL film isotherm (Figure 2a) occurs at $\approx 24 \, \text{Å}^2$ MMA on water at 12 °C or 21 °C, while the OCDME film (Figure 2b) shows the critical surface pressure at a lower MMA of $\approx 18 \, \text{Å}^2$ on water at 12 °C. The OCDME film isotherm (Figure 2b) on water at 21 °C does not show a pronounced critical surface pressure compared to the surface pressure versus area isotherms of OCDME at 12 °C or OCDOL at 21 °C or 12 °C.

2.1.1. Influence of End Groups on Maximum MMA for Crystallization

The BAM images in Figure 2 illustrate the crystal morphologies observed in the OCL films withheld for $\approx 2 \, \text{h}$ on water at 12 °C or 21 °C, at constant MMA of 22, 18, 15, 12 or 8.5 Å². At the given MMAs, all OCL films show formation of crystals except the OCDME film held at an MMA of 22 Å². Here, the OCDOL film is compressed to just above its critical surface pressure, while the OCDME film is slightly below the critical condition. The absence of crystallization in the OCDME film after several hours at 22 Å² shows that the shifted critical surface pressure is not of kinetic origin. Rather, the methacrylate end-groups increase the nucleation barrier for OCL chains at the air–water interface. We emphasize that the difference is not an effect of the $M_n$, since OCDOLs with a $M_n$ of 3500 g mol⁻¹ have a very similar crystallization behavior in Langmuir films when compared to OCDOLs with a $M_n$ of 8000 g mol⁻¹.[17] At the air–water interface, there might also be an influence of the central diol unit used as polymerization initiator. The OCDME has a diglyme unit, which is more hydrophilic than the butadiol used for OCDOL, which could contribute to the higher nucleation barrier by anchoring the chains to the interface and preventing the desorption of segments required for crystallization. Yet, this significantly higher nucleation barrier of OCDME correlates well with the bulk properties, where bulk OCDME has a lower $T_c$ of 18 °C, while bulk OCDOL has a $T_c$ of 29 °C, which agrees to a previous study using ethylene glycol initiated oligomers.[21]

2.1.2. Influence of End Groups on Crystal Habits

The morphology of OCDME crystals is characterized by a parallelogram shape with wavy edges (Figure 2d–7–12), whereas the hydroxy end capped OCL crystals have smoother edges and are less elongated (Figure 2c–1–6). The lateral shape of PCL crystals is determined by the prevalence of (110) and (100) growth sectors. Striations which run outward from the single crystal center, in (110) sectors are continuous and run parallel to the boundaries between the sectors (110) and (100). Striations in (100) sectors are not elongated but granular and non-continuous, and are less pronounced.[24] These sectors differ in viscoelastic properties[24] and can be identified as dark and bright areas in the BAM image of the roughly hexagonal OCDOL crystals (Figure 2c). The thermal stability of (100) sectors was found...
to be lower than the one of (110) sectors by other authors.[24] This suggests that optically darker sectors in the BAM images, which melt at lower temperature are (100) growth sectors (see inset in Figure 2a; and Figure S4, Supporting Information). The elongated shape of the OCDME crystals suggests a prevalence of (110) sectors, in agreement with the generally slightly higher $T_m$ of these crystals at the air–water interface. The greater lateral size of the OCDOL crystals indicates that the prevalence of (110) sectors in OCDME crystals is due to a reduction of the growth rate of (100) sectors in response to the methacrylate end groups. This observation is supported by the inset in Figure 2b where one of the (100) growth sectors is missing from the OCDME crystal.

2.1.3. Influence of Crystallization Temperature on Number Density and Size

OCL films on water at 12 °C (Figures 2c-4–6 and 2d-10–12) show higher number of crystals per unit area, but of smaller crystal size, compared to OCL films on water at 21 °C (Figures 2c-1–3 and 2d-7–9). This dependence of lateral size and number density on crystallization temperature is also seen in the OCDME film at MMA 8.5 Å², but not apparent at MMA 15 Å² (Figure 2d). In OCDOL films at a water temperature of 21 °C, the number of crystals per unit area increases with lowering of crystallization MMA, whereas such a trend is hard to identify for the other cases. However, under all conditions, the crystals appear laterally bigger at lower MMA, indicating that the growth rate or duration increases with crystallization surface pressure or decreasing MMA.

2.2. Crystallization, Melting, and Recrystallization of OCDOL and OCDME Films

Figure 3 shows the typical plot of surface pressure and temperature as the function of time during a crystallization–melting–recrystallization experiment at the air–water interface. At the constant temperature of the water subphase (12 °C or 21 °C), spread OCL molecules are compressed (increase of surface pressure; typical OCL Langmuir isotherm) to a specific MMA (8.5 Å²) and withheld for 2 h (stabilization of surface pressure). For melting of the partially crystalline OCL film, the water is heated at a constant rate (Figure 3a,b), and the melting temperature range of the partially crystalline OCL film lying on the water surface is identified using Figure 2.
the Brewster angle microscopy (see Figure S4a,b, Supporting Information). On the water surface, at \( T_{\text{m,onset}} \), melting begins in the partially crystalline film where the crystals observable as bright regions in the BAM images start to disappear (Figure 3c-2 and 3d-5). For the OCDOL crystals, the growth sectors appearing darker melt first (see Figure 3c-2). At \( T_{\text{m,end}} \), melting ends where the BAM image shows absence of any crystalline bright regions (see Figure S4, Supporting Information). The molten OCL film at the air–water interface is recrystallized by cooling the water subphase (Figure 3c-3,d-6). During the cooling of the water subphase, at recrystallization temperature (\( T_{\text{rec}} \)) the recrystal-lized entities start to appear as bright regions in the BAM (see Figure S4, Supporting Information), and the film is withheld for 30 mins to allow for recrystallization (Figure 3a,b). The water is cooled further to the initial isothermal crystallization temperature \( T_c \). Here, the surface pressure remains approximately constant over time, indicating that there is no driving force for further crystallization in partially recrystallized OCL. To identify thickness; topography and \( T_m \) at the air–solid interface, Langmuir–Schaefer transfers to silicon solid substrates are carried out in separate experiments, both of as-crystallized OCL films, as well as of partially recrystallized OCL films (Figures 4–6).

### 2.3. Relation of Crystal Thickness with Crystallization MMA and \( T_c \)

In Figure 4, the graph and the AFM images of transferred OCL films illustrate the effect of crystallization conditions (MMA or \( T_c \)) on the lamellar thickness and morphology. Clearly, the inverse crystal's thickness is directly proportional to the crystallization MMA, that is,

\[
\frac{1}{\text{Crystal thickness}} \propto \text{Crystallization MMA} \propto \text{Film area} \tag{1}
\]

In general, for an incompressible film:

\[
\frac{1}{\text{Film thickness}} = \frac{\text{Film area}}{\text{Film volume}} \tag{2}
\]

This finding suggests that for these ultrathin films, the crystal thickness is directly proportional to the film thickness prior to crystallization. Interestingly, the slope is identical for all conditions and end groups. This even includes recrystallization upon cooling, except for OCDOL crystals formed at 12 °C, where the crystal thickness depends much stronger on the film area. While there is an onset surface pressure for crystallization (critical surface pressure \( \pi^* \)), for OCDOL at both crystallization temperatures and OCDME at 12 °C, the surface pressure \( \pi \) does not increase beyond \( \pi^* \). Yet, there is a pronounced impact of the MMA, indicating that the film thickness rather than surface pressure, controls the crystallization behavior. The idea of a zero growth layer thickness is in line with the constant surface pressure observed after a certain crystallization period (Figure 3a,b). Here, the layer has reached its minimum layer thickness required for crystallization. If such a zero growth layer thickness did not exist, crystallization would continue until the whole film is crystalline.

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Figure 3. Plot of surface pressure and temperature during a) OCDOL and b) OCDME crystallization, melting, and recrystallization experiment. BAM images (scale bar = 100 µm) c) OCDOL and d) OCDME films acquired at different temperatures and time points. The heating to \( T_m \) leads to an increase in surface pressure. Upon cooling to \( T_{\text{rec}} \), the layer recrystallizes at nearly constant surface pressure. The surface pressure returns to its initial value upon cooling to the initial temperature (\( T_c \)).
The crystallization temperatures (12 °C or 21 °C) of OCL film at the air–water interface largely affect the morphology and number of crystals while the effect of $T_c$ (12 °C or 21 °C) on the crystals thicknesses difference is small ($\pm 0.5$ to 1 nm). There is a clear trend in the lateral crystal dimensions, which increase with decreasing MMA. As observed in bulk polymer crystallization, lowering of the isothermal crystallization temperature at the air–water interface to 12 °C results in a larger nucleation density and slightly reduced

**Figure 4.** Inverse crystal thickness as a function of mean molecular area (MMA) of OCL crystallization at the air–water interface. a) Trends for both as OCDOL (solid lines) and OCDME (dashed lines) films are represented. Selected topographical AFM images of Langmuir–Schaefer transferred b) OCDOL and c) OCDME at different conditions of crystallization and recrystallization.

**Figure 5.** Gibbs–Thomson plot of inverse OCL crystal thickness on function of melting temperature endpoint at the a) air–water interface and b) air–solid interface. Dependence of temperature of OCDOL (straight line) and OCDME (dashed line) to the inverse crystal thickness is represented. c) Gibbs–Thomson plot of recrystallization temperature as a function of inverse OCL crystal thickness at the air–water interface.
The lateral size of the crystals is smaller (Figure 2c,d) at lower crystallization temperature of 12 °C. This is probably due to a higher crystal number density. The higher nucleation density is also indicated by OCDME compression isotherms where a dip is observed at 12 °C, but not at 21 °C (Figure 2b).

The morphology of films of OCDOL (Figure 3c-3) and OCDME (Figure 3d-6) recrystallized at the air–water interface differ from the crystallized film (Figures 3c-1 and 3d-6) but the overall aspect ratio of the crystals is preserved upon recrystallization. These in situ observations by BAM are substantiated by AFM investigation of crystallized and recrystallized OCL films transferred to silicon surfaces (Figure 4b). AFM images of the partially recrystallized OCL films from the water surface show that the morphology and thickness of the recrystallized structures (Figure 4b-3) is different from the crystals prior to melting (Figure 4b-2). Except for the OCDOL film crystallized at 12 °C, in all the OCL films, the recrystallized structures are thicker than the melted OCL crystals, since recrystallization occurs at higher temperatures than crystallization upon compression. The partially recrystallized OCDOL film (Figures 3c-3 and 4b-3) shows presence of connected lamellae, small and large crystals, while the partially recrystallized OCDME film has crystals with protruding lateral lamellae (Figures 3d-6 and 4c-6). It is generally expected that the recrystallized structures are different from as-crystallized structures. By definition, there is no chain-overlap in a monolayer, and hence, there are no entanglements. The lowest MMA of 8.5 Å² corresponds to no entanglements. The lowest MMA of 8.5 Å² corresponds to no chain-overlap in a monolayer, and hence, there are no entanglements created when compressing the monolayer to that state. When single crystals grow from this almost non-entangled film, the chains will cross-over during attachment or back-folding. That means that the layer created by melting the single crystals contains more entanglements than the layer before crystallization, and hence, recrystallization proceeds under more constricted conditions than the first crystallization, which explains the disrupted crystal shapes.

2.4. Relation of \( T_m \) and \( T_{rec} \) with Crystal Thickness, Crystallization MMA, and \( T_c \)

The dependence of the melting temperature of lamellar structures on their thickness is described using the Gibbs–Thomson relation,

\[
T_m = T_m,\infty \left[ 1 - \frac{2 \sigma}{l h_f(T_{m,\infty})} \right] 
\]

where \( T_{m,\infty} \) is the melting temperature of infinitely thick crystals, \( \sigma \) is surface free energy, and \( h_f \) is the enthalpy of fusion. The \( T_m,\infty \) of the oligomers, OCDOL and OCDME used here is in a range where the bulk melting temperature still increases with \( M_n \), albeit very weakly.[21] While \( M_n \) (OCDME) is lower than the \( M_n \) (OCDOL), the Gibbs–Thomson equation is valid for each molecular weight fraction independently. Also, the crystal thickness in our experiments was not affected by the chain length, since the average contour length of the molecules here was around 40 nm (OCDME) or 70 nm (OCDOL). A Gibbs–Thomson plot of \( T_m \) versus inverse crystal thickness (Figure 5), shows that the \( T_{m,\infty} \) of partially crystalline OCL films on the water or solid surface is indeed proportional to the inverse crystal thickness, that is,

Crystal \( T_{m,\infty} \) at air–water or air–solid interface \( \propto \frac{1}{\text{Crystal thickness}} \)

The slope of the Gibbs–Thomson plot is much higher for the OCL films on the water surface (Figure 5a) compared to the OCL films on the solid surface (Figure 5b). Also, the stabilities are inverted on the solid substrate, with OCDME crystals showing a substantially lower \( T_m \) than the OCDOL crystals. The melting temperature is on average roughly 10 °C lower. The \( T_m \) in part accounts for this, with the equilibrium melting point of OCLs with a \( M_n \) of 4000 g mol⁻¹ being about 6 °C lower than the equilibrium melting point of the OCL with a \( M_n \) of 8000 g mol⁻¹.[20]

A second Gibbs–Thomson plot is constructed for the recrystallized structures (Figure 5c), where again all materials and conditions exhibit the same behavior except for the OCDOL film crystallized at 12 °C, where the crystal thickness decreases much stronger with \( T_{rec} \). In the OCDOL films crystallized at 12 °C, with lowering of crystallization MMA, the crystal thickness increases but the increase in lateral size is less compared with other crystallization conditions (Figure 2c,d). This perhaps...
leads to the anomaly of obtained slopes of Gibbs–Thomson plot for OCDOL films crystallized at 12 °C (Figure 5).

2.5. Dependence of $T_m$ and $T_{m,\infty}$ of OCL Films on the Interface Type

Figure 6 describes the dependence of melting/recrystallization temperature on the functional end groups (hydroxy or methacrylate) and crystallization conditions (MMA or $T_f$) of OCL films at different surfaces (water or solid silicon substrate). At the air–water interface, the temperature where the most stable crystals in OCDOL and OCDME films melt ($T_{m,\infty}$), decreases linearly with the MMA. This is expected since

$$T_m \sim - \frac{1}{T_{m,\infty}} \sim -\text{MMA} \quad (\text{Equations } (1) \text{ and } (3))$$

There is a good agreement between materials and conditions on the dependence of $T_{m,\infty}$ on the mean molecular area before crystallization, except for OCDOL at 21 °C, which shows a lower dependence of $T_m$ on MMA. The recrystallization temperature decreases linearly with the MMA of the film, and therefore with the thickness of the molten layer prior to recrystallization. This implies that the layer thickness influences the thermodynamics of crystallization, with thinner layers requiring greater undercooling to crystallize. Then, the thinner crystals formed in more undercooled Langmuir films are also less stable.

The temperature where the crystals with the lowest stability melt depends only weakly on the MMA of crystallization, which agrees with the idea that the crystal thickness decreases with the thickness of the amorphous layer. When the crystals grow, the thickness of the amorphous layer decreases, resulting in thinner crystals. Crystallization stops at a “zero growth” layer thickness, resulting in a minimum crystal thickness and hence $T_m$. The “zero growth” layer thickness decreases with temperature, resulting in a $T_{m,\infty}$ that depends on $T_f$, but not MMA. The slight dependence of $T_{m,\infty}$ on the MMA shown in Figure 6a might also be an artifact of the finite heating rates, meaning that the laterally larger crystals formed at lower MMA disappear at slightly higher temperature. At the air–water interface, $T_{m,\infty}$ of OCL films is higher than the $T_{m,\infty}$ of OCDOL films, potentially because of the different stabilities of (110) and (100) sectors. Yet, on solid surfaces, the $T_{m,\infty}$ is lower for the films than for the films, which agrees more with the bulk situation where the higher $M_n$ leads to a higher melting temperature.

Altogether, OCL ultrathin films prepared under different crystallization conditions, melt at higher temperature ranges on solid surface (45 °C to 60°C) compared to films on water surface (20 °C to 45 °C). Also, the dependence of the melting temperature on the crystal thickness is much lower at the air–solid interface. By extrapolating the $T_m$ versus the inverse crystal thickness to infinite crystal thickness, we obtain the equilibrium melting temperatures $T_{m,\infty}$ for both conditions. At the air-water interface, $T_{m,\infty}$ is between 42 °C to 48 °C while at the air–solid interface, $T_{m,\infty}$ is between 53 °C (OCMED) and 65 °C (OCDOL). These values are smaller than the $T_{m,\infty}$ of PCL in bulk, which are 75 °C for a $M_n$ of 8000 g mol$^{-1}$ and 69 °C for 4000 g mol$^{-1}$.[25] Thus, both water and bulky end-groups lead to a lowering of the equilibrium melting point. The melting point in ultra thin films on silicon is lower than the melting point in bulk as well, despite the adsorption to the solid substrate. From the plot of the recrystallization temperature versus inverse crystal thickness (Figure 5c), we determine the crystallization temperature of infinitely thick PCL crystals at the air–water interface $T_{c,\infty}$. This temperature is at ≈55 °C for the OCDOL and at ≈70 °C for the OCDME. The finding that $T_{c,\infty}$ is smaller than $T_{m,\infty}$ is in agreement with crystallization in bulk.[26] Altogether, crystallization and melting in ultra thin films at the air–water interface follows similar laws as in bulk, albeit with generally lower transition temperatures. The slope of $T_m$ versus inverse crystal thickness at the air–water interface (Figure 5a) is much greater than at the air–solid interface (Figure 5b). Since $T_{m,\infty}$ is also smaller, this suggests that the ratio of surface energy to crystallization enthalpy is much greater at the air–water than at the air–solid interface. This is because the amorphous OCL forms a 2D solution at the air–water interface, but the crystalline phase is not stabilized, leading to a decrease of the enthalpy of crystallization.

Considering the interfaces, OCL films melting is achievable at lower temperature range on the water surface than at the solid surface by a temperature, which is roughly 20 °C lower (Figure 6). During the melting of OCL ultrathin film on a substrate, the crystals may preferentially start to melt at the points of contact between the crystal and the substrate. On the water surface, OCL chains may have large point of contacts due to the fluidic and penetrable nature of small water molecules. Besides, during heating of the substrate for melting the OCL film, the degree of molecular motion within the aqueous liquid subphase is higher compared to the bulk solid substrate. On the solid surface with the OCL film, points of contact between the OCL chains and the rigid flat solid surface may be fewer but of strong adhesion forces, which modify the melting process of the crystals. Therefore, on the solid surface, the OCL crystals melting (Figure 6b) proceeds in a constrained environment, with a lower supply of crystalline chain folds into the neighboring amorphous phase. The crystalline polymer chains on the water surface can melt and recrystallize (Figure 6a) easily due to a larger mobility in comparison with the polymer chains on the solid surface. During heating of the LS transferred OCL films at the air–solid surface, droplets of melt are formed inside the periphery of the crystals (not illustrated here; see Figure S5, Supporting Information). During cooling of the melted OCL film on the solid surface, the $T_{m,\infty}$ is not identifiable since the partially recrystallized OCL film does not visually differ from the melted OCL film at the air–solid interface.

Regarding the role of end groups, the most obvious one is the change in crystal habits because of the different prevalence of (100) and (110) growth sectors. The greater sterical requirements of the methacrylate groups may also account for the wavy edges observed in some of the OCL methacrylate crystals. The uniform edges of OCDOL crystals suggest that hydrophilic but lower molar mass hydroxy groups essentially pose minimal steric hindrance in OCL chain folding for crystallization. The higher nucleation barrier for the methacrylate end-capped molecules is apparent from the crystal number density and the higher critical surface pressure $\pi^c$. The higher $T_{m,\infty}$ shows that a greater degree of supercooling is indeed required to nucleate these crystals. Compared to the OCDOL central unit, the OCDME central unit is more polar but also of a higher molar mass. According to literature, the central diol unit plays
OCDME might increase the nucleation barrier for crystallization at the air–water interface, the more hydrophilic central unit in the OCDOL might increase the nucleation barrier for crystallization by anchoring the chains to the water phase, along with the bulkier methacrylate end groups.

An interesting observation is the inversion of the crystals’ stability at the air–water interface and the air–solid interface. A potential explanation is the ability of functional end groups to act as diluents for the polymer melt, which results in a lowering of the melting temperature. Here, it seems intuitive that hydroxy groups are stronger diluents in an aqueous environment, whereas methacrylate groups are hydrophobic and more effective in air.

### 3. Conclusion

Partially crystalline ultrathin films of OCL diol and OCL dimethacrylate were prepared at the air–water interface at different film mean molecular areas (22, 18, 15, 12 or 8.5 Å²) and aqueous subphase temperatures (21 °C or 12 °C). Melting/recrystallization was studied for partially crystalline OCL ultrathin films directly at the air–water interface, and also at the air–solid interface after Langmuir–Schaefer transfer to a silicon substrate. Thickness and topographic evaluation was performed for as-crystallized and recrystallized OCL films on silicon substrates. Methacrylate groups affected the chain packing and led to a higher prevalence of (110) growth sectors in OCL single crystals grown at the air–water interface.

In comparison to OCL spherulites in bulk, for investigating thermal properties in ultrathin films, crystallization temperature, end group functionalization, central core group, Mₘ, but also the single crystal’s thickness is taken into account. The melting/recrystallization temperatures of OCL diol and OCL dimethacrylate single crystals at the air–water interface or air–solid interface were proportional to the inverse crystal thickness, in agreement to the Gibbs–Thomson equation. The Mₘ corrected equilibrium melting temperature at the air–solid interface occurs at temperatures, which are about 10 °C lower than those in bulk, while the equilibrium melting temperature at the air–water interface is about 25 °C lower than in bulk. While a critical surface pressure πₐ for crystallization was observed, both the lateral crystal size and thickness increased with initial film thickness, which is defined by the MMA for isochoric crystallization, while the initial crystallization surface pressure was almost identical.

The methacrylate groups lead to a considerable lowering of the melting point only in the absence of water. These are important considerations when, for example, using OCL crystals as thermal switches for medical applications. A recrystallization process is noticed with measurable parameters only at the air–water interface, where the recrystallized structures are thicker than the melted crystals, as they form at higher temperatures. This study highlights not only the precisely controllable parameters at the air–water interface for preparing single crystals with defined thermal transitions, but also the importance to take the presence of water into account when using PCL crystals as thermal switches in aqueous environments. In future, we will exploit the high density of functional end groups at OCL crystal surfaces to construct stimuli responsive nanostructured materials with adjustable switching temperatures.

### 4. Experimental Section

**Materials:** Oligo(ε-caprolactone) diol (OCDOL, trade name CAPA 2803, Solvay Caprolactones, Warrington, U.K.) and oligo(ε-caprolactone) dimethacrylate (OCDME, Sigma–Aldrich) were used without any further purification. OCDOL basic characterization was described in detail previously.

**Table 1** summarizes the bulk material characteristics of the OCDOL and OCDME used in this study. The Mₘ was determined by gel permeation chromatography (GPC). The set up consisted of a mixed D column (600 mm × 7.5 mm, Polymer Laboratories Ltd.), a T60A dual detector, and a refractive index detector (Shodex RI-101, Showa Denko, Japan). Chloroform (HPLC grade, Roth) was used as the eluent at a flow rate of 1.0 mL min⁻¹. The rate of heating or cooling was 10 K min⁻¹. Thermal properties were determined from the first cooling and second heating cycle run. The shift of end group functionalization determined by ¹H NMR analysis is within the limits of experimental error of signal integration. The shift of Mₘ to higher values in GPC than ¹H NMR can be related to fractionation of the reaction products by precipitation. The temperature range of Tᵣ and Tᵢ is estimated by extrapolation of slopes of exotherms and endotherms from DSC measurement.

The methacrylate groups lead to a considerable lowering of the melting point only in the absence of water. These are important considerations when, for example, using OCL crystals as thermal switches for medical applications. A recrystallization process is noticed with measurable parameters only at the air–water interface, where the recrystallized structures are thicker than the melted crystals, as they form at higher temperatures. This study highlights not only the precisely controllable parameters at the air–water interface for preparing single crystals with defined thermal transitions, but also the importance to take the presence of water into account when using PCL crystals as thermal switches in aqueous environments. In future, we will exploit the high density of functional end groups at OCL crystal surfaces to construct stimuli responsive nanostructured materials with adjustable switching temperatures.

### Table 1. Bulk characteristics of OCL samples.

| Sample | Mₘ(GPC) [g mol⁻¹] | M₀ (¹H NMR) [g mol⁻¹] | End group functionalization (¹H NMR) [%] | PDI (GPC) | Tᵣ (DSC) [°C] | Tᵢ (DSC) [°C] |
|--------|------------------|-----------------------|------------------------------------------|-----------|----------------|----------------|
| H      | 8300             | 7900                  | 95 ± 3                                   | 1.2       | 29 ± 4.5       | 56 ± 4         |
| L      | 5900             | 4300                  | 85 ± 2                                   | 1.2       | 18 ± 4.5       | 39 ± 4         |
Langmuir trough (KSV NIMA, Finland) placed on an active vibration isolation system (Haloyonics variobasic 40, Accurion, Germany) within a laser safety cabinet. A water bath, circulating exteriorly below the trough’s teflon base, controlled the temperature of the filled liquid subphase in the Langmuir trough. BAM images were recorded in real time on Langmuir trough with ellipsometer nanofilm ep3 (Accurion, Göttingen, Germany) equipped with a high performance CCD camera, a 10× magnification lens with a maximum lateral resolution of 2 μm, and a 658 nm class IIIB laser source. π was measured by the Wilhelmy technique with a calibrated sensor placed at the center between the barriers. The trough was cleaned thoroughly with ethanol (HPLC grade; Bernd Kraft, Duisburg, Germany) followed by chloroform (HPLC grade, Roth, Germany). The deionized water filled in Langmuir trough was obtained by a Milli-Q Gradient A-10 water purification system (Millipore, 18.2 MU cm, toc < 4 ppb). The deionized water was filled and removed at least three times. By monitoring the surface pressure, the purity of the Langmuir trough and the aqueous subphase was controlled. In the final aqueous subphase, while closing the barriers, the total change of the surface pressure was below 0.2 mN m⁻¹. For all OCL samples, the chloroform stock solutions had concentrations in the range of 0.2 to 0.4 mg mL⁻¹. The solution was applied drop-wise onto the air–water interface using a microsyringe (Hamilton Co., Reno, NV, USA). The chloroform was allowed to evaporate for 30 min before the start of OCL film compression. The rate of compression and expansion of monolayer was 10 mm min⁻¹. The Langmuir trough software (KSV NIMA) used the input variables of spread amount of OCL solution at air–water interface, trough surface area, and temperature. The trough was cleaned thoroughly with ethanol (HPLC grade; Bernd Kraft, Duisburg, Germany) followed by chloroform (HPLC grade, Roth, Germany). The deionized water filled in Langmuir trough was obtained by a Milli-Q Gradient A-10 water purification system (Millipore, 18.2 MU cm, toc < 4 ppb). The deionized water was filled and removed at least three times. By monitoring the surface pressure, the purity of the Langmuir trough and the aqueous subphase was controlled. In the final aqueous subphase, while closing the barriers, the total change of the surface pressure was below 0.2 mN m⁻¹. For all OCL samples, the chloroform stock solutions had concentrations in the range of 0.2 to 0.4 mg mL⁻¹. The solution was applied drop-wise onto the air–water interface using a microsyringe (Hamilton Co., Reno, NV, USA). The chloroform was allowed to evaporate for 30 min before the start of OCL film compression. The rate of compression and expansion of monolayer was 10 mm min⁻¹. The Langmuir trough software (KSV NIMA) used the input variables of spread amount of OCL solution at air–water interface, trough surface area, and M, of repeat unit (ε-caprolactone; 114 g mol⁻¹) to calculate the OCL film MMA. The output curves show relationships between MMA, surface pressure, temperature, compression speed and time. Under isothermal conditions, the OCL films were compressed and held at different MMA's (crystallization MMA) and OCL crystallization was observed in real time by BAM. Under constant compression rate, the surface pressure point at which OCL crystals first started to appear in the BAM was defined here as the critical surface pressure πc. For crystals melting, aqueous subphase was heated at the rate of 2 °C ± 0.5 °C min⁻¹ until a clear BAM image without any crystalline structures is observed. For recrystallization, the aqueous subphase was cooled, and withheld for 30 min at the temperature Trec where the recrystallized structures could be observed in BAM images.

Cry stalization Study at Air–Solid Interface: Langmuir–Schafer Films: Partially crystalline, and recrystallized OCL films at different MMA's were transferred onto silicon substrates (Plano GmbH, Germany) by Langmuir–Schafer (LS) method. Briefly, acetone cleaned silicon substrate was horizontally brought in contact with the partially crystalline or recrystallized OCL film on the water surface. The melting point of LS transferred partially crystalline OCL film on the water surface was cooled, and withheld for 30 min at the temperature Trec where the recrystallized structures could be observed in BAM images.

Atomic Force Microscopy: The topography of the OCL films in air was performed using a Nanowizard AFM (JPK Instruments, Germany) in the intermittent contact mode at 21 °C ± 0.5 °C. Tips used were made of silicon (285 KHz resonance frequency; 42 N m⁻¹ force constant; Nano World). To determine the crystal thickness from AFM images, WSxM 5.0 software was used[28]. Polarized Optical Microscopy with Temperature-Controlled Stage: Polarized optical microscopy was performed at Zeiss Axio Imager A1m microscope (Carl Zeiss, Jena, Germany) equipped with crossed polarizers and a Linkam LTS 350 heating stage (Linkam Scientific Instruments Ltd., Tadworth, United Kingdom). 40× magnification objective (Zeiss A-plan) was used in reflection mode with the temperature rate change of 2 °C ± 0.4 °C min⁻¹ in air.

Statistics Experimental Errors and Error Considerations with Respect to Instrumentation: All OCL films melting and recrystallization experiments at air–water interface or air–solid interface were performed more than two times. At the air–water interface, the systematic error range of the surface pressure sensor was ±0.3 mN m⁻¹ and temperature sensor was ±0.2 °C. The experimental error in spreading polymer solution and environmental impurities led to irregularity in OCL film MMA measurement by ±1 Å². The instrumentation error of rate of heating or cooling at the air–water or air–solid interface was less than ± 0.5 °C min⁻¹. For thermal analysis of bulk material, the DSC had an instrumentation error of ± 0.5 °C. The statistical error of the crystal thickness was calculated by mean deviation of the values obtained from at least three AFM images (see Figure S6, Supporting Information). The statistical error of the melting temperature is given as a temperature range between the points where the first signs of melting and complete melting were observed.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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