Different paths to explore confined crystallisation of PCL

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http://dx.doi.org/10.1016/j.eurpolymj.2012.10.001

III. N. Sanandaji, V. Bretzler, S. Schmelter, M.S. Hedenqvist and U.W. Gedde. Confined space crystallisation of poly(\(\varepsilon\)-caprolactone) in controlled pore glasses, Submitted to Euro Polym J.


Abstract

In this work, different paths to confined crystallisation of poly(ε-caprolactone) (PCL) have been explored. Innate confinement effects due to the presence of bulky end groups were shown to affect crystalline characteristics for strictly monodisperse ε-caprolactone oligomers. The interaction between end groups and end groups, as well as that between end groups and ε-caprolactone repeating units, created an obstacle for unfolding the crystal structures that had initially formed even at the high-temperature limit of crystallisation where crystallisation occurred over hundreds of hours. Very rapid X-ray imaging of the in situ crystallisation process showed that rapid shifts in the unit cell occurred during the first minute of crystallisation due to the difficulty of fitting the bulky end groups in a stable unit cell. Confinement effects also arose when polymer chains were crystallised in systems with small pore sizes. For linear poly-ε-caprolactone, chains confinement depended mainly on the dimensionalities of the pores. Linear polymers with \( M_n = 10\,000 \) and 42 500 were strongly inhibited from forming crystal structures in 10 nm pore systems, but not hindered in 23 nm pore systems. Linear polymers with \( M_n = 80\,000 \) also experienced limited confinement in the 23 nm pores. A star-shaped oligomer with four arms of approximately \( M_n = 1\,000 \) each even experienced confinement in 290 nm pores, although having smaller molecular size and radius of gyration compared to the linear chains. The innate confinement created by the challenge of packing four arms amplified the effect of physical confinement. Another limitation was created on the crystallisation process by solving PCL in supercritical CO\(_2\) and depositing during extremely fast phase transfer to gas-like state. The formed structures were limited by the very low temperature that resulted from the phase change and by the rapid evaporation of the solvent. These limitations resulted in entrapment of crystal structures in metastable phases. As a consequence, crystals of hitherto unreported rectangular form were observed as well as the common six-sided form. The former crystals had considerably lower melting point compared to the latter. X-ray analysis showed that two sets of lattice constants existed, supporting the notion of entrapment in metastable phases. Another way of achieving confinement was precise deposition of droplets in the pikolitre volume range of highly dilute solutions. The microcrystals which formed were confined by both the low polymer content in each droplet and by the time constraint on crystal formation that arose by the rapid evaporation of the small droplets. Confinement led to entrapment into metastable phases, evident by the presence of unusual eight-sided and rectangular crystals.
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1. List of symbols and abbreviations of chemicals

**Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPG</td>
<td>Controlled Pore Glasses</td>
</tr>
<tr>
<td>$L_p$</td>
<td>Long period</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Crystalline layer thickness</td>
</tr>
<tr>
<td>NPG</td>
<td>Non-porous glass beads (NPG)</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Starting temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallisation temperature</td>
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<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>$V_C$</td>
<td>Percentage volume of crystalline part</td>
</tr>
<tr>
<td>$W_c$</td>
<td>Mass crystallinity</td>
</tr>
<tr>
<td>$W_{c\text{-corrected}}$</td>
<td>PCL mass crystallinity</td>
</tr>
<tr>
<td>wt</td>
<td>Weight</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>Amorphous density</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Crystalline density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Surface energy/unit area</td>
</tr>
<tr>
<td>$\sigma_e$</td>
<td>Fold surface free energy /unit area</td>
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</table>

**Chemicals**

<table>
<thead>
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<th>Chemical</th>
<th>Description</th>
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<tr>
<td>Bn</td>
<td>Benzyl</td>
</tr>
<tr>
<td>CL</td>
<td>$\varepsilon$-Caprolactone oligomer</td>
</tr>
<tr>
<td>PCL</td>
<td>Poly($\varepsilon$-caprolactone)</td>
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2. Introduction

2.1. Purpose of this study

The complex process of polymer crystallisation can be influenced by innate characteristics of the polymer molecules, such as end group composition, the number of arms and chain length. It is influenced by environmental factors such as crystallisation temperature, physical confinement and limitations on the amount of polymeric material available in the vicinity of forming crystals. Both innate characteristics and environmental factors can limit the ability of polymer chains to organize in ways that would otherwise be preferred. The purpose of this work has been to explore different paths to confine the process of crystallisation and examine how this affects crystalline features such as crystal morphology, melting behavior and molecular packing.

This work also relates to early metastable phases. Early stages of crystallisation have attracted the focus of scholars recently since they provide insight into the more elaborate behaviors of polymers during crystallisation that are not addressed by simple models. In 1991 Rastogi et al. [1] convincingly showed that a metastable phase for polyethylene existed at elevated pressure but below the triple point. This mobile hexagonal form of the polymer preceded the stable crystalline form. Studies of metastable phases have continued since. Early metastable phases are difficult to study since they are short lived. By trapping polymers in said phases one might gain the window of opportunity to study them more in depth. A central question in this work has been whether various strategies to confine the process of crystallisation can lead to entrapment into early metastable phases.

2.2. Polymer crystallisation

Crystallisation in polymers systems has been debated by various scholars since polymer crystallisation was first mentioned by Staudinger in 1927 [2]. Based on electron diffraction and electron microscopy findings Keller was the first who observed the crystal lamella, the basic element in polymer crystallisation. In 1957 Keller [3] showed that thin single crystals of polyethylene can be grown from dilute solutions. He discovered that the long polymer chains
were more or less regularly folded between the upper and lower lamella surfaces. In the same year Till [4] and Fisher [5] reported independently of each other that platelet-shaped single crystals were obtained by cooling dilute solutions of polyethylene.

These findings were the first proofs that regular flexible-chain polymers crystallize in chainfolded lamellae. It was soon discovered that lamellar crystals of other polymers also exhibited chain folding and that chain folding was an essential feature of crystallisation from the molten state. Keller realized that the spherical structures (spherulite) visible by electron microscopy arose due to branching and splaying of the basic lamellar structure. The detailed mechanism of spherulite formation was to be revealed some 30 years later. Bassett et al. [6] then discovered that the giant screw dislocation generated two or more diverging crystallizing arms, which were capable of obtaining spherical symmetry.

It has since become generally recognized that as soon as a polymer crystal with favorable thickness to with ratio is formed, it tends to rearrange. This occurs since the structure is thermodynamically unstable and can lower its internal energy by lowering the amount of fold-chain surface per unit volume. Polymer crystals thus tend to change shape with time at temperatures between the crystallisation temperature and the melting point. Barham et al. [7] have been able to show that the long period of polyethylene crystals doubled microseconds after the onset of crystallisation. The process of crystal thickening is illustrated in Fig. 1.

![Fig. 1. Schematic representation of the mechanism of crystal thickening. Núñez [8]](image)

In 1961 and 1962 Hoffman and Lauritzen [9,10] presented their theory for growth of chainfolded crystals based on nucleation theory for polymer crystallisation from solution and from the melt. The Hoffman-Lauritzen model is built upon the idea that an increase in the activation barrier leads to the characteristic exponential law for the variation of the crystallisation time with the crystallisation temperature.
Since the beginning of the 1960s, the Hoffman-Lauritzen theory and several modifications and extensions of it have dominated the scientific debate regarding the process by which polymers crystallize. The activation barrier has to be surmounted when placing a nucleating first stem into the growth face. The crystal growth rate is determined by this “secondary nucleation” step. The resulting structure is the one which develops with the highest rate. According to the Hoffman-Lauritzen model the maximum development rate is reached for a crystal thickness just above the stability limit of the crystal.

The Hoffman-Lauritzen theory can explain many experimental observations and can also be used to calculate key quantities such as crystal thickness and crystal growth rate as a function of temperature. However the model, which acknowledged the fact that crystals are far from equilibrium and thus exhibit metastability, is based on simplifications. According to the model, the formation of the secondary nuclei occurs by adsorption of a single stem with some unspecified disorder. The formation of the tertiary nuclei occurs by the immediate ordering to perfect crystalline state. The Hoffman-Lauritzen model has been criticized and built upon by a number of researchers.

Point and Dosiére [11] have, for example, suggested flaws in the model when it comes to explaining the kinetics of polymer crystallisation. Particularly the observation of ordered structures at very early times has led to the development of new theories. Sadler [12] constructed an alternative model which works for rough growth faces. An elementary step that is introduced in this model is a reversible detachment and attachment of short-chain sequences. Calculations based on the Sadler model suggest that the growth face explores many different configurations and that a high entropic activation barrier controls the rate of growth. The model proposed by Sadler, similarly to the Hoffman-Lauritzen model, suggests that the lamellar crystallites grow directly into the entangled melt.

In an article published in 1997, Hoffman and Miller [13] developed a flux-based surface nucleation model that is concerned with the nature of polymer chains in close detail. This paper amongst others deals with the variation of the initial lamellar thickness, undercooling, the origin of the lateral surface free energy $\sigma$, the fold surface free energy $\sigma_e$, “quantized” chain folding at low molecular weight and the generation of nonadjacent events such as tie
chains. It also explains the origins of various crystalline regimes and associated crystal growth rates.

A number of studies have broadened our understanding by focusing on how molecular defects can alter crystallisation conditions. Martínez-Salazar and Balta-Callaeja [14] have for example shown that the presence of defects or short branches causes the unit cell to expand. Sanmartín et al. [15] have shown that not only the final unit cell, but also the complex pathways through which ordered domains are formed, are affected by the presence of chain-defects. As our knowledge about polymer crystallisation grows, research efforts have also focused on the early stages of crystallisation.

2.3. Early stages of crystallisation

Models dealing with polymer crystallisation have evolved considerably since polymer crystallisation was first mentioned in 1927. However, they still tend to be focused on later stages of crystallisation and cannot fully explain observations relating to very early stages. During recent years, a number of scholars have attempted to provide insight into the complex behaviors of polymers during early crystallisation that are not addressed by traditional models.

Kymaraswamy et al. have [16] studied the early stages of crystallisation in a polydisperse isotactic polypropylene during and after a brief interval of shear. They found that the lamella seemed to grow from a central thread until they impinged about 100 s after cessation of shear to form the dense crystalline structure in the skin.

Early stages of crystallisation of polyethylene were also studied by Wang et al. [17] via simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS). Short-range density fluctuations with periodic spacing ranging from 40 to 80 nm were detected by SAXS before the identification of 3D crystal ordering by WAXS. This and similar studies have indicated that the spindonal decomposition due to chain conformation in the molten state may act as a precursor to crystallisation. Another interpretation is that the early
stages of crystallisation follow the classical nucleation and growth behavior with a simple Avrami expression.

Pogodina et al. [18] have, by performing dynamical mechanical experiments on four isotactic polypropylenes, shown that the early stages of crystallisation can be thought of as a process of physical gelation. Albrecht et al. [19] studied crystallisation of polyethylene in early stages by time-resolved SAXS and determined the lamellar thickness at the various stages of crystallisation. It was found that a gradual transition occurred from the initial stage with single lamellae to the formation of stacks of lamellae. This was accompanied by a continuous and logarithmic growth of the crystallite thickness with time. The theories on early stages discussed above assume a multistep process from the entangled melt via different metastable structures to the final polymer crystal. What then do we know about metastable phases?

2.4. Metastable phases

The concept of metastability was first discussed by Ostwald over 100 years ago [20], when he in 1897 wrote that "[I]n the course of transformation of an unstable (or metastable) state into a stable one the system does not go directly to the most stable conformation (corresponding to the modification with the lowest free energy), but prefers to reach intermediate stages (corresponding to other metastable modifications) having the closest free energy to the initial stage". As later noted by Keller and Cheng [21] a metastable phase possesses a local free energy minimum, but is not at the global stable equilibrium. This simple idea is illustrated in Fig. 2. Constraints of size, dimensionality, order and symmetry can lead to circumstantial metastability according to the researchers. In addition, they note that metastable behavior can be observed in phase transformations impeded by kinetic limitations along the path to thermodynamic equilibrium.

A number of studies have confirmed the presence of metastable phases in polymer systems. Rastogi et al. [1] have showed the existence of a metastable phase for polyethylene at elevated pressure and below the triple point. This mobile hexagonal form of the polymer preceded the stable crystalline form. Another convincing evidence of the existence of metastable phases originated from a paper by Ungar and Rastogi [22] where they showed size-induced phase
transformation from metastable hexagonal to stable crystalline form of poly(trans-1,4-butadien). As the lamellar thickened, a transition from hexagonal phase to monoclinic form occurred. A conformational energy model for poly(ethylene terephthalate) was set up by Hedenqvist et al. [23], which in molecular simulations indicated a metastable phase for the polymer.

![Fig. 2. Simple illustration of the concept of metastability. Keller and Cheng [21]](image)

Trasz et al. [24] have published a study on the influence of crystallisation conditions on the contact layer morphology of high-density polyethylene crystallized on graphite. They found that the morphology of the polyethylene contact layer consisted of striated, ribbonlike structures organized in domains in which the striations followed the same direction. It was suggested that the parallel alignment of the chains along one direction over large areas in many stacked lamellae might indicate the existence of a mobile hexagonal mesophase in the melt (at least on the graphite surface) before its crystallisation.

Magonov et al. [25] performed a similar study where they looked at the annealing of single crystals of polyethylene on graphite. Structural transformation was observed with increasing temperatures. Transformation began at the edges and in a few central locations of the crystals and spread as annealing temperatures increased. Annealing of re-crystallized polyethylene led to flattening and widening of the strands, which transformed into stacks of molecular ribbons. The researchers noted that the polyethylene crystallized and re-crystallized on graphite might
be in the hexagonal phase – at least so far as this definition can be applied to molecular ordering within one or a few molecular layers.

Recently a general model for polymer crystallisation including the presence of metastable phases has been suggested. Strobl [26] has published a paper where he, based on experiments on several polymer systems, suggested a new model of polymer crystallisation where the formation and growth of the lamellar crystallites is considered a multi-step process involving intermediates. The initial step is suggested to be the creation of a mesomorphic layer that spontaneously thickens up to a critical value. The layer then solidifies through a cooperative structural transition and a granular crystalline layer is produced. In the last step this layer is transformed into homogeneous lamellar crystallites.

Sirota [27] has built upon the work done by Strobl. Sirota has argued that the granular structure of the crystal lamella in itself is a fingerprint of the transient mesophase into which a lamella originally grows, as well as its conversion to the stable crystalline form. Cheng has published a work presenting a new theory building on previous experimental work. According to Cheng [28] the existence of metastable systems have so far been mainly attributed to the free energy barrier delaying the transition from the initial to the final phase and causing supercooling or superheating of the growth rate competition between different pathways.

This traditional view causes us to deal with one metastable stage at a time, rather than focusing on interaction between various metastable states on different length scales. Cheng [28] has proposed that there exists a wide range of metastable states in polymers on different length scales. The metastability is according to Cheng critically determined by the phase size and by the dimensionality. The fact that the transient state of a phase is strongly size dependent has also been argued for in an overview of the research field written by Rastogi [29].

2.5. Indications of metastable phases during PCL crystallisation

The presence of metastable phases has also been suggested in early stages of PCL crystallisation. By using bright-field and dark-field diffraction contrast methods of
transmission electron microscopy (TEM) Iwata et al. [30] indicated the existence of nanoscopic blocks (striations) in single crystals of PCL. It was shown that both tightly- and loosely chain packing regions exist in one lamellar crystal, supporting the idea that PCL lamellar crystals consist of nano-order micro-crystals. The existence of loosely chain-packing regions was indicated by observation of enzymatic degradation behavior.

Wurm et al. have [31] utilized dielectric relaxation experiments to point to the presence of a pre-existing partly ordered phase in PCL. Due to low contrasts of scattering experiments, the evidence from such experiments indicating the formation of pre-ordered structures during polymer crystallisation is speculative. Relaxation experiments, however, probe motion in the sample and are independent on density contrast. As material is transformed from liquid to solid state during crystallisation, motions typical for a liquid become impossible in a crystal and do not longer contribute to the measured signal.

Pre-ordered structures are also expected to give rise to some changes in mobility because of the changes in conformation on pre-ordering. The experiments conducted by Wurm et al. [31] during isothermal crystallisation of PCL indicated effects long before a change in crystallinity could be detected, which suggested the idea of pre-order in the polymer melt before crystal formation. Previous studies thus point to PCL being an appropriate model for studies of metastable phases during early stages of crystallisation.

2.6. Confined crystallisation in nanoporous systems

A number of recent studies have focused on crystallisation in nano-confined environments. Nano-confinement is often achieved by using crystalline-amorphous diblock copolymers [32]. It has been observed that with increased dimensionality of confinement, the reduction of crystallisation rate tends to be more severe [33–36]. Another way to achieve spatial confinement is to utilize controlled pore glasses (CPGs), which contain nano-scale pores. The first studies exploring confinement in CPG pores were focused on the behaviour of organic solids and liquids housed in the pores. Jackson and McKenna [37,38] showed that the melting point of non-polar organic solids confined in CPGs increased with increasing pore diameter.
McKenna et al. [37–39] showed that pore confinement decreased the glass transition temperatures of organic liquids. Park and McKenna [40] observed two glass transitions of polystyrene-o-terphenyl solutions soaked into CPGs. The low temperature transition appeared at temperatures below the bulk glass transition temperature, and it increased with increasing pore diameter. The high temperature transition occurred above the bulk glass transition temperature and it was assigned to an interacting layer at the pore surface. Yung and Sindee [41] studied crystallisation of a cyanurate-trimer in CPG pores, and showed that the confinement decreased the cold crystallisation temperature. The crystallisation kinetics slowed down due to confinement, but, surprisingly, the Avrami exponent remained at 2 both for bulk and nano-confined samples.

Hamilton et al. [42] crystallised glycine in CPGs. Glycine persisted for at least one year in the β crystal form when confined in a CPG with pore diameters less than 24 nm, whereas in CPGs with 55 nm pores the β crystals slowly transformed into the α crystals. Rengarajan et al. [43] studied crystallisation of the polymorphic acetaminophen in the confinement of CPGs. X-ray diffraction showed the presence of three polymorphs of acetaminophen housed in the CPG pores and it was shown that the nano-confinement affected the stability of the different polymorphs.

The effects of nano-confinement on polymorphism and thermal stability of the different phases of low molar mass substances are thus fairly well known. However, crystallisation of polymers housed in the nano-pore systems has not yet been studied extensively. In particular, little has previously been published on the crystallisation kinetics of confined samples.

2.7. PCL single crystal previously observed during confinement and non-confinement

Previous studies of PCL, utilizing a range of different crystallisation conditions, have clearly showed the preference for forming six-sided single crystals, i.e. the crystals displayed six lateral phases, in addition to the two fold surfaces. Such crystals grown from hot toluene or propanol solutions were observed already by Bittiger et al. [44] in 1970. Brisse and Marchessault [45] observed multilayer six-sided PCL crystals grown from nitrobenzene solution by using the self-seeding method. Itawa et al. [46,47] made similar observations on
single crystals of PCL fractions grown from dilute \( n \)-hexanol solutions. The layers were shown to emanate from screw dislocations.

Núñez et al. [48,49] observed similar structures formed by single crystals of linear PCL and star-branched polyesters with PCL arms grown from \( n \)-hexanol or \( n \)-butanol using the self-seeding technique. Crystals based on star-branched polymers had the same basic form as crystals grown from linear PCL but with more irregularities such as curvatures, steps and niches. Beekmans and Vancso [50] cast solutions of PCL dissolved in chloroform on glass slides, melted the films after drying, and re-crystallised these on hot-stage AFM. They observed multilayer six-sided crystals, with curved edges. The crystals were so curved that they were almost oval in shape.

Mareau and Prud'homme [51] spin-coated solutions of PCL in tetrahydrofuran, melted the films and re-crystallised them on a hot-stage while studying them in-situ by AFM. Films with thicknesses of 120 nm and 200 nm showed multilayer six-sided crystals, with screw dislocations. Films with 30 nm or 60 nm thickness exhibited monolayer six-sided crystals. Even thinner films (15 nm) displayed distorted six-sided structures, with truncations of the \{110\} sectors. Finally, 6 nm thick films formed even more distorted structures, which resembled distorted parallelograms more than distorted six-sided structures.

It is thus well established that PCL under various conditions tends to form six-sided crystal structures, with the exception being distorted structures formed by very thin films. These structures are illustrated in Fig. 3. A relevant question in this work has been whether various strategies for limiting the ability of polymer chains to organize in ways that would otherwise be preferred can lead to formation of different single crystal shapes or not.
Fig. 3. Sketches of the six-sided crystal (left) with four \{110\} sectors and two \{100\} sectors, commonly observed in previous works on PCL single crystals, as well as a distorted parallelogram structure (left) with two \{110\} and two \{100\} sectors, observed for crystals grown from very thin films. The crystals are viewed along the \(c\)-axis.

2.8. Confined crystallisation of PCL

Early metastable phases are inherently difficult to study due to their ephemeral nature. One way of “trapping” polymers in metastable phases, thereby allowing for detailed studies of these phases, might be crystallisation in confined environments. Núñez et al. [52-55] have previously conducted studies on confined space crystallisation of PCL molecules. These studies focused on star-branched PCL samples.

The crystallizing elements in the star-branched oligomers are fixed, slowing down crystal rearrangement and creating an innate confinement effect on crystallisation. The dendritic cores had a profound effect on the crystallisation of the linear PCL arms attached to them, leading to higher equilibrium melting point, moderately lower crystallinity, slower crystal rearrangement and a greater tendency to form spherulites in comparison with linear PCL. However, the crystal phase after complete crystallisation was the same for star-branched and linear PCL samples.

This current work has been inspired by the work done by Núñez et al., but has relied on different strategies to achieve confinement. The first strategy was to utilize the innate physical confinement present in a set of uniquely monodisperse \(\varepsilon\)-caprolactone (CL) oligomers. The oligomers utilized were linear but had different sets of end groups, with various bulkiness and
hydrogen bonding potential. The end groups present affected the aptitude of the oligomers to pack in ordered crystal structures. Also the lengths of the oligomers varied, which was useful since end group effects could be expected to more strongly affect shorter rather than longer molecules.

The second strategy was to crystallize CL oligomer chains in nano-sized pores with different pore sizes and a narrow pore size distribution. The pores physically confined crystallisation of linear CL chains of various sizes, as well as a star-shaped CL oligomer. These studies have revealed a range of interesting findings relating to confinement, packing arrangement and early stages of crystallisation.

The third strategy was to solve PCL in supercritical CO₂ and deposit the solution during extremely fast phase transfer from supercritical to gas-like state. It has previously been shown by amongst others Weiming et al. [56] that supercritical CO₂ changes the crystallisation behavior of polymers such as syndiotactic polystyrene. In the present work the structures formed by depositing PCL solved in supercritical CO₂ onto silica plates was investigated. In effect very small droplets were ejected in which the solvent very quickly evaporated. The polymer structures that were formed on the silica surface where the droplets landed were limited in their crystallisation process by the very low temperature which arose from the phase transfer as well as the very rapid evaporation of the solvent.

The fourth strategy involved precise deposition of droplets in pikolitre volume range of highly dilute solutions. The microcrystals that formed were confined by both the time constraint on crystallisation that arose due to the rapid evaporation of the small droplets and by the low polymer content in each droplet. Unique crystal structures could be shown to arise on the surfaces created by both the third and the fourth strategy, confirming that the confinement strategies indeed affected the resulting crystals.
3. Experimental

3.1. Materials

The monodisperse caprolactone oligomers used in this work were synthesized by Kenichi Takizawa et al. [57] through an exponential growth strategy. Synthesis was conducted using Benzyl (Bn) ester as the protective group of the carboxylic acid group and t-Butyldimethylsilyl ether as the protective group of the hydroxyl group. Since an inert atmosphere was not required for the reactions, a robust and efficient synthetic strategy could be developed resulting in strictly mono-disperse oligomers. The structures of the studied samples with different chain ends A and B and repeating units \( n \) are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( A )</th>
<th>( B )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-CLn-B</td>
<td>( t )-Butyldimethylsilyl (^b)</td>
<td>Bn(^c)</td>
<td>4, 8, 16, 32, 64</td>
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<tr>
<td>O-CLn-B</td>
<td>OH</td>
<td>Bn</td>
<td>4, 8, 16, 32</td>
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<tr>
<td>T-CLn-H</td>
<td>( t )-Butyldimethylsilyl</td>
<td>H</td>
<td>4, 8, 16, 32</td>
</tr>
</tbody>
</table>

The oligomers, denoted “STAR-4000” by Hakala et al. [58], have a \( M_n \) of 4270 as measured by NMR, a \( T_g \) of 212 K, exhibit two melting peaks at 319 and 324 K, respectively and have a melting enthalpy of 70 J/g. Three poly(\( \varepsilon \)-caprolactone)s with different molar masses, \( M_n = 10 \) kDa (PCL10), 43 kDa (PCL43) and 80 kDa (PCL80) (the three polymers had \( M_w / M_n = 2.0 \pm 0.1 \)), and non-porous glass particles (NPG) with diameters less than 106 nm were obtained from Sigma Aldrich.
Table 2. Characteristics of the controlled pore glasses used

<table>
<thead>
<tr>
<th></th>
<th>CPG1</th>
<th>CPG2</th>
<th>CPG3</th>
<th>CPG4</th>
<th>CPG5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore diameter(^a) (nm)</td>
<td>10 ± 1</td>
<td>23 ± 2</td>
<td>53 ± 4</td>
<td>130 ± 10</td>
<td>290 ± 10</td>
</tr>
<tr>
<td>Pore volume(^b) (mL g(^{-1}))</td>
<td>0.86</td>
<td>1.07</td>
<td>0.87</td>
<td>0.85</td>
<td>1.17</td>
</tr>
</tbody>
</table>

\(^a\) Measured by Hg intrusion  
\(^b\) Calculated based on a silica density of 2200 kg m\(^{-3}\)

Controlled pore glasses (CPGs) and information relating to the sample were supplied by Dr. Wolfgang Haller at NIST, USA. Linear PCL polymers crystallized in the CPGs, as well as non-porous glass beads (NPG) with diameter ≤ 106 nm, were obtained from Sigma Aldrich. Star-shaped PCL oligomers, also used for crystallisation in CPG/NPG systems, were supplied by Hakala et al., who have synthesized the hydroxyl-terminated molecules. The properties of the CPGs are shown in table 2. Ultra-pure carbon dioxide (99.9%) used in the RESS technique was supplied by Scan gas-Strandmöllen AB, Denmark.

3.2. Controlled Pore Glass systems

The CPG and NPG were pretreated in order to promote wetting by organic solvent. First the glasses were cleaned in chloroform for 24 h. Thereafter they were soaked in hexamethylenedisilazane for 24 h to convert the surface hydroxyl groups to trimethylsilyl groups. The glasses were then washed with chloroform on a filter five times. Samples were prepared by solving the oligomers in 1-butanol and mixing the resulting solution with 5 mg treated CPG or NPG particles in a 100 µl aluminum DSC pans.

The CL/1-butanol solutions had a caprolactone concentration of 15 wt. percent and were heated to 358 K to solve the oligomers during stirring. In CPG samples an amount of CL/1-butanol solution was added theoretically enough to fill 40 percent of the total pore volumes. For the NPG samples, which lacked pores, an amount of sample was added corresponding to the average amount added to the five different CPG systems. After mixing the DSC pans were sealed with aluminum lids punctured with three holes.
The holes allowed for the 1-butanol to evaporate as the pans were stored in 353 K ovens for at least 12 h. In addition, pristine oligomer samples were obtained simply by adding CL material to aluminum pans. Conventional differential scanning calorimetry (DSC) experiments were performed with a Mettler-Toledo DSC820 calorimeter and a nitrogen flow of 50 mL/min. The crystallisation progress was monitored for the different systems at various times and at various temperatures.

### 3.3. RESS technique

The RESS process stands for “rapid expansion of a supercritical solution”. When using this technique, samples were prepared by dissolving 2.50 mg PCL in 100 µL chloroform and transferring the solution to a home-built stainless steel view cell holding 20 mL. The view cell was heated using a heating tape coded ELW-HS (IHP International Heating Products AB, Sävedalen, Sweden).

Temperature control was accomplished by a cascade controller model 3504 (Invensys Eurotherm AB, Malmö, Sweden). When the temperature of the view cell was stable at 313 K, pressurized CO$_2$ was delivered by a syringe pump model 100DX (Teledyne Isco, Inc., Lincoln, USA) to the cell, resulting in a system with CO$_2$ as the main solvent and 0.1 vol.% chloroform as a co-solvent. The outlet tubing from the pump was coiled and placed in a water bath to heat the CO$_2$ before it entered the vessel. The set-up is illustrated in Fig. 4.

The PCL solution with supercritical CO$_2$ and the small amount of chloroform was mixed with a magnetic stirrer at 250 bar pressure and 313 K for 60 min, after which the valve of the 0.1 mm diameter nozzle (Thar Technologies Inc., Pittsburgh, USA) was opened and the solution was sprayed onto a silica plate. The distance between the nozzle and the silica plate was 120 mm. The temperature at the silica surface during spraying was measured using a CIR568-L0 dual-laser IR thermometer (Metris Instruments, LLC, USA).
Inkjet deposition principles and setup

Inkjet printing, a digital printing technology, is increasingly being applied in scientific fields such as nanotechnology, tissue engineering and polymer engineering [59,60] where it can be used for the precise deposition of pL volumes of suspensions or solutions in well-defined patterns. This “direct-writing” can be accurately controlled by micro-electro-mechanical ink-dispensers, which in turn are controlled by computers and high-speed electronics. In this work, the application of Inkjet printing is explored in a new context, namely to study confined crystallisation.

Inkjet deposition not only makes it possible to “print” structures where crystal growth is limited by the small amount of material present in each droplet, but also leads to an additional confinement effect due to the evaporation of the pikolitre size droplets within a few seconds. This rapid evaporation constrains the process of crystal formation, limiting the ability of the polymer chains to assemble into crystalline structures while in solution, and it may therefore prove valuable for trapping the polymer in a metastable phase, a precursor to crystallisation.
Another advantage of the Inkjet technique is that the non-contact deposition method is free from contaminants, which might otherwise influence crystal formation and particularly the initiation of crystal formation.

Inkjet printing is based on the creation of an acoustic pulse, which ejects liquid droplets through a nozzle. The pulse can be generated by either thermal or piezoelectric means [61]. In the instrumental setup used in this work, the latter technology was used to eject droplets of precise size. The dispenser together with the fluid reservoir flask and the piezoelectric mechanism is sketched in Fig. 5. Fluid ejection was accomplished using a MD-K-140 piezoelectric dispenser obtained from Microdrop Technologies, Norderstedt, Germany.

1-Butanol solvent was filtered before mixing with PCL and heated to 363 K in order to dissolve the polymer while it was being stirred. The solutions were subsequently diluted in several steps to obtain concentrations as low as 10^{-6} gL^{-1}. The solutions were again filtered before Inkjet dispensing, in order to ensure samples with a very high purity. Impurities would not only have affected crystal growth but could also have led to clogging of the nozzle.

The core of the dispenser head consisted of a glass capillary surrounded by a tubular piezoelectric actuator. One end of the capillary was formed as a 51 µm nozzle. A voltage pulse caused a contraction of the piezoelectric actuator and built up a pressure wave that propagated through the capillary and pushed fluid outwards. The kinetic energy of the acoustic wave was partly converted to the surface energy of the droplet formation, and partly to the kinetic energy of the free-flying droplet. When the amount of kinetic energy transferred outwards was greater than the energy needed for droplet formation, 110 pikolitre droplets were ejected with a velocity of 2 ms^{-1}.

The ejected droplet flew freely through the air and in practice could be very accurately placed on a substrate located just below the dispenser head. The substrates were silica plates, cleaned by ethanol, Milli-Q water and plasma followed by vacuum drying. The sample stage on which the substrates were placed could be accurately moved in the x, y and z directions as necessary. Depending on the choice, either single droplets or arrays of multiple droplets were dispensed. Dispensing was carried out at a constant relative humidity of 45 ± 3 %, and at constant
temperature, 296 ± 1 K. Both the fluid reservoir and the dispenser head were heated to 343 K during dispensing.

Fig. 5. Sketch of the Inkjet dispenser (right) and of the piezoelectric mechanism (left). The piezoelectric mechanism is based on the application of a voltage pulse (left, second image from top) leading to the propagation of a pressure wave through the capillary (left, third and fourth image from top). The wave transfers the liquid to the nozzle (left, fifth image from top) and finally leads to formation of a droplet when the kinetic energy transferred outwards is greater than the surface energy required to form a droplet (left bottom image). A = Cord to heat control box. B = Vent. C = Cord to dispenser control box, controls dispensing and temperature at dispenser head. D = Dark grey area shows a protective shell including heating elements, which also extends around the flask containing the polymer solution.

Fig. 6 illustrates the droplet formation shortly after dispensing. As the droplet flew through the air it acquired a spherical shape. Each dispensing step, from the creation of the acoustic pulse to the formation of a spherical droplet, occurred so precisely that when stroboscopic images were taken at the same frequency of droplet formation, the viewer could almost be fooled to think that she or he were studying a single droplet hovering in mid-air.
Fig. 6. Sketch of the process of droplet formation as it appears shortly after dispensing. The droplets adopt a spherical shape during their flight.

3.5. Non-isothermal crystallisation

All non-isothermal crystallisation experiments were conducted directly in the DSC oven. The samples were initially heated from starting temperature ($T_s$) to melting temperature ($T_f$) at 10 K min$^{-1}$. Melting temperature varied at ca. 340 – 348 K for the various oligomers, being higher for the longer ones. Samples were held for 3 min at $T_f$ to erase thermal history and subsequently cooled at various constant cooling rates. Thereafter, the samples were again heated from $T_s$ to $T_f$, at various heating rates. Data collection occurred during the second heating period and during the cooling period. Cooling rates varied between 0.5 – 30 K min$^{-1}$ whilst heating rates varied between 0.5 – 70 K min$^{-1}$.

3.6. Isothermal crystallisation

Isothermal crystallisation experiments were conducted in order to attain samples for DSC analysis as well as for SAXS and WAXS analysis. Isothermal crystallisation experiments for
DSC analysis were carried out in the DSC apparatus when crystallisation times were shorter than one day. Samples were heated from $T_s$ to $T_f$ at 10 K min$^{-1}$ and subsequently held at $T_f$ for 3 min to erase thermal history. Thereafter, samples were cooled at 60 K min$^{-1}$ to crystallisation temperature ($T_c$) and held for various crystallisation times ($t$).

When crystallisation times were longer than one day, isothermal crystallisation for DSC samples were performed in temperature controlled ovens. The samples were tightly sealed in 40 µL aluminum pans and melted in an oven for five minutes. Thereafter, the samples were immediately transformed to a second oven set at required $T_c$. After various periods of isothermal crystallisation, samples were quenched with liquid nitrogen.

Samples for SAXS analysis were obtained through isothermal crystallisation in ovens as described above, the only difference being that samples were inserted in quartz tubes rather than aluminum pans and also quenched in ice water rather than liquid nitrogen. Isothermal crystallisation experiments for WASX analysis were conducted in oil baths held at constant temperatures. Samples were initially melted in one oil bath and thereafter transferred to a second oil bath and held there for various times (30 min, 1 h, 1 day or 5 days). The samples were subsequently quenched in ice water.

Samples for WAXS analysis were also crystallized in situ. In these cases WAXS data was collected for samples at either 12 s or 61 s intervals whilst going from melt to crystallisation temperature and subsequently whilst isothermally remaining at crystallisation temperature. The experiments were performed at temperatures where the samples crystallized slowly, making it possible to focus on the early stages of crystallisation. Heating and spraying of liquid nitrogen allowed for temperature control.

### 3.7. DSC and TGA analysis

Thermal examinations of samples were performed isothermally and non-isothermally with a Mettler-Toledo differential scanning calorimetry (DSC) 820 apparatus. The thermal system apparatus utilized nitrogen as purge gas and had a cooling device. For each experiment
1.1 ± 0.1 mg sample was used. Regular calibration was performed by measuring enthalpy of fusion and onset melting temperature of a pure Indium sample.

The polymer contents in the different impregnated CPG systems were determined by TGA using a Mettler-Toledo TGA/SDTA 851 equipment. The mass loss was recorded during heating from 300 K to 800 K at a rate of 5 K min⁻¹ in oxygen gas environment. The gas flow rate was 50 mL min⁻¹.

3.8. SAXS and WAXS analysis of samples not deposited on surfaces

Before analysis with WAXS/SAXS samples were incorporated into 1.5 mm quartz capillary tubes supplied by Hampton Research. SAXS measurements were performed using a custom-built intermediate small angle diffractometer (2-circle) in the Materials Research Laboratory at UCSB, USA. The following specs were used: Bent graphite monochromator, Cu radiation at 1.54 Å, 0.8 mm x 0.8 mm beam size at the sample position, 18 cm diameter Mar image plate detector, ~ 10⁷ photons/second flux.

WAXS measurements were gathered with three different apparatus. Measurements of samples quenched after 30 min – 5 days were performed in the Materials Research Laboratory at UCSB, USA. A custom-built wide angle diffractometer (4-circle) with the following specs was used: OSMIC Confocal Maxflus focusing mirror monochromator, 1.0 mm x 1.0 mm beam size at the sample position, Cu radiation at 1.54 Å, Mar image plate detector, ~ 10⁸ photons/second flux.

In situ WAXS data with 61 s between each measurement were gathered in the Arrhenius Laboratory at the University of Stockholm, Sweden. An Oxford diffraction Xcalibur 3 X-ray device utilizing Mo radiation at 0.71 Å was used. Temperature control was achieved with sensitivity 0.1 K through heating and spraying of liquid nitrogen. Lastly, in situ WAXS data with 12 s between each measurement were gathered in Maxlab, Sweden. A synchrotron radiation source with 0.908 Å wavelength was used in Maxlab. Temperatures were chosen where samples crystallized very slowly, and temperature control with sensitivity 0.1 K was achieved through heating combined with spraying of liquid nitrogen.
3.9. SAXS and WAXS analysis of samples deposited on silica surfaces by RESS

Ultra-grazing-incidence wide angle x-ray scattering experiments were carried out with the incidence close to 0° at P03 MINAXS beamline, PETRA III, DESY, Germany. The X-ray wavelength was 0.0957 Å, and the 2D scattering pattern were collected by the pilatus 300k detector (pixel size 172 × 172 (µm)²) with a sample detector distance of 180 mm. Beam damage was minimized by measuring at different positions over the sample. The average scattering pattern was obtained by summing all the single shot scattering patterns. Image processing incorporated software dpdak 3.0 integrated with Fit2D.

The line profile was extracted by azimuthal integration over 15°, and the zero degree incidence angle was determined by the half maximum photon beam intensity through rocking scan and height scan. As a reference, the same PCL polymer was crystallized in the normal phase in small quartz capillaries by heating and quenching. This sample was measured with an Oxford diffraction Xcalibur 3 x-ray device, with Mo radiation at 0.711 Å.

3.10. Atomic force microscopy (AFM)

The AFM used for non-hot-stage measurements (Digital Instruments, Dimension 3100) was equipped with a surface analysis upgrade for intermodulation AFM (Intermodulation Products AB), a multi-frequency dynamic force measurement method which rapidly and accurately extracted the nonlinear response of the oscillating cantilever. This response was analysed using a contact-mechanics model for the nonlinear tip-surface force, in order to determine the model parameters that fitted the measured response.

In this way, parameter maps of the surface were generated, colour-coded, and projected onto a two-dimensional rendering of the surface topography. The Derjaguin-Muller-Toporov (DMT) model was used to determine the effective Young’s modulus $E^*$, which is due to the mutual deformation of the round tip and the semi-infinite flat surface, at each point where AFM measures have been taken. $E^*$ is a measure of the contact stiffness, but the measured force
depends on the tip radius and on the contact geometry. A tip radius of 10 nm was assumed in the calculation to extract an effective $E^*$ at each point on the surface.

Hot-stage experiments were performed under ambient conditions using a Multimode microscope with NanoScope III controller (Veeco). The instrument was equipped with a J-scanner. The maximum scan size was 100 (µm)². Commercially available Si-cantilevers (NANOSENSORSTM) with resonance frequencies of 204 – 497 kHz and force constants of 10 – 130 Nm⁻¹ according to the manufacturer were used.

Measurements were carried out in the tapping mode, always using the largest set point ratio to minimize interactions between the tip and the sample. A high temperature accessory provided by Veeco was used. It enabled heating from ambient to 523 K. Height, amplitude and phase images were acquired simultaneously. The high temperature experiments were carried out as follows: the sample stage and the tip were heated from room temperature to melting temperature in steps of 5 K. The tip was always withdrawn from the sample during heating. Tip engagement was achieved only after the selected temperature had been reached and remained stable. Images were acquired under isothermal conditions.
4. Calculations and computer modeling

4.1. Calculations

Relative amounts of mass crystallinity \((w_c)\) for the monodisperse samples shown in table 1 were calculated based on DSC data according to Equation 1. The degree of crystallinity of the samples was affected by end groups. Bulky segments in the end groups likely do not crystallize, reducing the overall crystallinity of the oligomers. This phenomenon decreases in relevance for overall crystallinity as the number of repeating units in the CL chains increase. In order to compensate for end group effects the mass crystallinity was studied as a function of the CL backbone excluding end groups. Values of CL mass crystallinity \((w_c\text{-corrected})\) were therefore calculated by dividing \(w_c\) with a correction factor representing the CL weight fraction in the molecule, i.e. excluding the end groups \(A\) and \(B\).

During calculations of \(w_c\) and \(w_c\text{-corrected}\) the following values were used: \(T_m^0=356.7\) K according to Núñez et al. \([53]\), \(\Delta H(T_m^0) = 135\) J/g according to Crescenzi et al. \([62]\) and values of \(C_p_a(t)\) and \(C_p_c(t)\) were given by ATHAS. Information regarding long periods \((L_p)\) in various fractions were given by SAXS experiments. The thickness of the crystalline layers \((L_c)\) were calculated by multiplying \(L_p\) with the percentage volumes of the crystalline parts \((V_c)\). \(V_c\) was calculated according to Equation 2 based on values of amorphous and crystalline densities of PCL \((\rho_a\) and \(\rho_c)\). The values of \(\rho_a\) and \(\rho_c\) were obtained from Crescenzi et al. \([62]\) as 1.081 g/cm\(^3\) and 1.20 g/cm\(^3\) respectively.

DSC and SAXS data were combined in order to calculate the surface energy \(\sigma\) according to Equation 3, where \(T_m^0\), \(\Delta H(T_m^0)\), \(\rho_c\) and \(L_c\) were obtained as described previously and \(T_m\) is measured as the melting point \((T_f)\) acquired from DSC data.
\[ W_c = \frac{\Delta H_f}{\Delta H_f(T_m^0) - \int_{T_i}^{T_m^0} C_{p_a}(t) - C_{p_c}(t) dt} \]  

(1)

\[ V_c = \frac{w_c}{w_c(1 - \frac{\rho_c}{\rho_a}) + \frac{\rho_c}{\rho_a}} \]  

(2)

\[ \sigma = \frac{L_c \cdot \rho_c \cdot \Delta H^0(T_m^0) \cdot (T_m^0 - T_m)}{2T_m^0} \]  

(3)

The crystallisation kinetics data taken at 312 K were analysed using the classical Avrami equation where \( v_c \) is the volume crystallinity attained at time \( t \), \( v_{c\infty} \) is the finally reached volume crystallinity, i.e. the volume crystallinity attained behind the crystal front, and \( K \) and \( n \) are parameters obtained by fitting Eq. (4) the initial stages of experimental crystallisation vs. time data; \( n \) is referred to as the Avrami exponent.

\[ \frac{1}{v_c} = \exp(Kt^n) \]  

(4)

### 4.2. Unit cell determination and data modeling

Unit cell determination was performed with the help of collaborating researcher Professor Emeritus Per-Eric Werner at Stockholm University. Peak positions and peak intensities were determined using the program PFILM [63], and the unit cell was determined by the powder indexing program TREOR [64]. In the trial phase cell dimensions up to 150 Å were studied.

Models of 8-, 16- and 32-mers with various combinations of terminal groups were built in ChemBio3D Ultra. Energy minimization was performed in the same program. Each model underwent several thousand steps of energy minimization before reaching equilibrium where energy no longer could be reduced through further iterations.
For each energy minimization experiment typically 37 molecules were placed in a model representing single layer ordering. Intermolecular distances were in most cases set to 5.0 x 7.5 Å and the molecules were ordered in zig-zag formation, approximating the unit cell determined experimentally for PCL by Bittiger et al. [65]. Modelling was performed both for systems where the molecules all had the same alignment and for systems where molecules had the opposite alignments compared to their closest neighbours.
5. Results and discussion

5.1. Influence of chain length and end groups on melting endotherms and folding

Very precise calorimetric data could be collected for the CL samples described in table 1, due to their monodisperse nature. The data showed that end group composition and chain length clearly influenced crystal formation. The shortest oligomers, with 4 repeating units, exhibited unimodal melting, with the highest recorded melting peak temperature strongly depending on the end groups: 257 K (T-CL4-B), 260 K (T-CL4-H) and 292 K (O-CL4-B). At full crystallisation at the highest possible crystallisation temperatures the 8-mers also exhibited narrow (melting range = 3 – 5 K) unimodal melting peaks at different temperatures depending on the end groups: 304 K (T-CL8-H), 308 K (T-CL8-B) and 327 K (O-CL8-B). As illustrated in Fig. 7 T-CL8-H also showed a very small melting peak at 299 K.

![Fig. 7. Melting endotherms for the CL₈ oligomers crystallized at highest possible crystallisation temperature. a = T-CL8-B, b = O-CL8-B, c = T-CL8-H.](image)

Due to their low melting point, SAXS data could not be collected at room temperature for the 4-mers, but however for the 8-mers that were solid at room temperature. The SAXS patterns appeared for all the studied samples as distinct rings showing at least three orders of the same periodic spacing (long-period). Two examples are shown in Fig. 8 and 9 respectively. The long periods recorded for the oligomers with 8 repeating units were 7.4 nm (T-CL8-B), 8.3 nm (T-CL8-H) and 13.8 nm (O-CL8-B). Thus, O-CL8-B formed double layers presumably by strong hydrogen bonding between the terminal hydroxyl groups. Similar structures have been
observed in long-chain carboxylic acids after crystallisation at high temperatures [66,67]. The difference in long period between the two other samples can be explained by a difference in the angle between the CL-stem and the normal to the crystal lamella (tilt angle) in order to house the large terminal groups of T-CL8-B.

**Fig. 8.** Left: 2D SAXS data from PCL8-O sample crystallized isothermally at 297 K. Right: Logarithmic plot of intensity of the same sample. Three peaks of integral ordering can be seen at 0.76, 1.61 and 2.44 inverse nm respectively, corresponding to a lamellar structure. A fourth peak can be observed at 1.15 nm and corresponds to an additional ordering, likely rectangular or slanted.

Fig. 10 shows that the melting of O-CL8-B after a long-term crystallisation at a lower temperature (297 K) is clearly bimodal with a distinct exothermic crystallisation peak between the two melting peaks. The dominant low-temperature peak is positioned at 316 K. The SAXS long period of this particular sample was 8.3 nm, suggesting extended-chain crystals. The transformation occurred during heating, as shown by the crystallisation peak at 321 K and the final melting peak at 324 K (notably 3 K lower than the recorded melting peak for the sample crystallized at 311 K). This may indicate the formation of double-layer crystals during heating. This double layered structure was not present at higher temperatures.
**Fig. 9.** Left: 2D SAXS data from T-PCL₈-H sample crystallized isothermally at 301 K. Right: Logarithmic plot of intensity for the same sample. Four peaks arranged in integral order can be observed at 0.76, 1.52, 2.28 and 3.04 inverse nm respectively, corresponding to a well defined lamellar structure.

**Fig. 10.** Melting endotherms for O-CL8-B crystallized at 297 K.
It is proposed that the double layer is due to the formation of hydrogen bonds between the terminal hydroxyl groups, which requires the accumulation of the hydroxyl groups on one side of the crystal lamella. This concept is illustrated in Fig. 11. Thus, it is suggested that the low melting crystal form consists of a random distribution of benzyl and hydroxyl groups on the crystal surfaces. The double-layer crystals observed in O-CL8-B oligomers were not found in any of the O-CL16-B or the O-CL32-B samples. However calorimetric data indicated that such structures were also formed by O-CL4-B oligomers. This might be explained by the fact that end groups influence overall molecular behavior more in shorter chains.

The melting point for the single-layer crystals of O-CL8-B (316 K) was greater than those of T-CL8-B and T-CL8-H (308 K and 304 K respectively). Furthermore, none of the other oligomers with 8 repeating units showed a bi-layered crystal structure. This indicates that hydrogen bonding do play a role in stabilizing also the single layer crystal of O-CL8-B. The T-CL8-H sample could potentially be stabilized by specific interaction between the carboxyl acid end groups whilst the T-CL8-B could be stabilized by interaction between adjacent benzyl groups by pi-stacking. The lower melting temperatures of these samples indicate that stabilization has been much more limited than in the O-CL8-B sample. This seems to be due to the t-butyldimethylsilyl groups (the T groups), with their bulky structures, prohibiting stabilizing interaction forms in the T-CL8-H and T-CL8-B samples respectively.

The 16-mers where unique in exhibiting two different crystallisation regimes: once-folded crystals at low crystallisation temperatures and extended-chain crystals at higher temperatures. The long period data obtained for samples crystallized at the higher temperatures for extended periods of time showed a gradual increase with increasing crystallisation temperature, from 15 nm at 312 K to 17 nm at 322 K. The highest value of 17 nm is in accordance with the long period of a stack of crystals with untitled chains, whereas the lowest value of 15 nm is consistent with a stack of crystals with CL-stems at a tilt angle of 28°.

Remarkably neither of the oligomers with 32 or 64 repeating units contained extended-chain crystals even at the high-temperature limit of crystallisation where crystallisation occurred over hundreds of hours. Instead the 32-mers exhibited once-folded structures whereas the 64-
mrs exhibited thrice-folded structures. The interaction between end groups and end groups, as well as that between the end groups and the CL oligomer units, evidently created an obstacle for the unfolding of the once-folded chains of the oligomers with 32 repeating units and for the thrice-folded CL chains of the oligomer with 64 repeating units.

Fig. 11. Proposed structures of low- and high-melting crystal forms of O-CL8-B.

5.2. Influence of chain length and end groups on PCL mass crystallinity

PCL mass crystallinity ($w_{c\text{-corrected}}$) typically increased for samples as crystallisation temperatures increased. At the same time longer crystallisation times were required in order to achieve high degree of crystallinity at higher temperatures. For example, for the T-CL32-H sample to reach a level of crystallisation at 322 K comparable to at 311 K, the time had to be increased by a factor of 32. In cases when compensations in increased time were not adequate, $w_{c\text{-corrected}}$ values decreased rather than increased with crystallisation temperature. For the shorter O-CLn-B samples ($n = 2, 4$ and $8$) the observed values of $w_{c\text{-corrected}}$ were around and sometimes above 100 percents. This depended on hydrogen bonds increasing the value of $\Delta H_f$ measured by DSC, so that it becomes incomparable to the value of $\Delta H(\int_{T_m}^{T_0} C_p_a(t) - C_p(t))dt$ used to calculate $w_{c\text{-corrected}}$. 

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As shown in Fig. 12, values of $w_{c\text{-corrected}}$ were highest for the shorter oligomers and only slowly decreased as the number of repeating units increased. As a comparison Núñez et al. found that the mass crystallinity of linear PCL decreased from around 60-80 percent for 20-mers to ca 55-65 percent for 60-mers at 273 K. A linear decrease in $w_c$ with increasing oligomer length was shown [53]. The overall CL crystallinity behavior observed in this work was similar to the observations by Núñez et al.

![Graph](image)

**Fig. 12.** Values of $w_{c\text{-corrected}}$ for T-CLn-H (black rhombuses), O-CLn-B (grey circles), T-CLn-B (light grey squares) and CLn-unP (white triangles) samples crystallised at 322 K. Crystallisation time varies between 300 minutes and 14 days.

By studying $w_{c\text{-corrected}}$ data it can readily be shown that the combination of the $t$-butyldimethylsilyl and carboxylic acid end groups present in T-CLn-H samples had a distorting effect on crystallisation. The T-CL2-H sample was difficult to crystallize. As shown in Fig. 13, for the T-CL4-H sample the value of $w_{c\text{-corrected}}$ rapidly fell by almost a factor of 10 as crystallisation temperature was decreased from 233 K to 261 K. Such an effect could not be observed for neither the O-CL4-B nor the T-CL4-B samples. Similarly, as shown in Fig. 14, the T-CL8-H samples were hindered from crystallizing by increasing crystallisation temperature in a clearly stronger way than the O-CL8-B and the T-CL8-B samples. This distorting effect decreased as the chain length was increased and could not be observed for the T-CL16-H and the T-CL32-H samples. This is explained by the fact that end groups influence overall molecular behavior less in longer chains compared to shorter ones.
Fig. 13. Values of $w_{c\text{-corrected}}$ for T-CL4-H (black rhombuses), O-CL4-B (grey circles) and T-CL4-B (light grey squares) samples crystallized at different temperatures. The crystallisation time for the samples shown varies between 120-720 minutes.

Fig. 14. Values of $w_{c\text{-corrected}}$ for T-CL8-H (black rhombuses), O-CL8-B (grey circles) and T-CL8-B (light grey squares). The crystallisation time for the samples shown varies between 300 minutes to 11 days.

5.3. Melting data for monodisperse CL oligomers

Fig. 15 summarizes melting enthalpy data for samples melted either after isothermal crystallisation for extended periods of time or after crystallisation during cooling at a constant rate of 10 K min$^{-1}$. The enthalpy difference data are normalized with respect to CL-content in each sample. The three series of oligomers with different end groups all obeyed the same basic pattern:
(i) A distinct maximum in melting enthalpy was obtained for the oligomers with 8 repeating units.

(ii) Melting enthalpies for isothermally crystallized samples and samples crystallized during a constant rate cooling were essentially identical for the oligomers with 4 and 8 repeating units.

(iii) The melting enthalpy for the longer oligomers (≥ 16 repeating units) was significantly lower for the samples crystallized during constant rate cooling than for those isothermally crystallized.

End groups clearly influenced the melting enthalpy. O-CLn-B oligomers showed a significantly higher melting enthalpy, particularly for the isothermally crystallized samples, than both T-CLn-B and T-CLn-H oligomers. The maximum value recorded, 150 J (g CL)^{-1}, was greater than the melting enthalpy of 100% crystalline PCL which, according to Crescenzi et al. [62], is 135 J (g PCL)^{-1}. This, along with the ability of O-CLn-B oligomers to form double-layered structures (amongst the 4- and 8-mers) illustrates the significant effect of end groups on crystal structure. Clearly, both the very high enthalpy and the ability to form double-layered structures depend on hydrogen bonding potential (coupled with the lack of bulky t-butyl(dimethyl)silyl groups which inhibited effective hydrogen bonding for the T-CLn-H oligomers).

The other two oligomer types, not exhibiting this extreme interaction, showed very high crystallinities for the oligomers with 8 repeating units: 90% (T-CL8-B) and 83% (T-CL8-H). This suggests that approximately one repeating unit out of eight remained amorphous. The oligomers with 4 repeating units showed lower crystallinity values than the oligomers with 8 repeating units: 72% (T-CL4-B) and 56% (T-CL4-H), indicating that roughly one repeating unit out of four remained amorphous.

The oligomers with 16 repeating units displayed extended-chain crystals and yet the crystallinities showed some depression with respect to those of the oligomers with 8 repeating units: 75% (T-CL16-B) and 80% (T-CL16-H). Hence, these data suggest that the end-groups had a stabilizing effect on the crystals. The further lowering in crystallinity in the case of the longer T-CLn-B oligomers can be attributed to chain folding: 69% (T-CL32-B; one fold) and 67% (T-CL64-B; three folds).
**Fig. 15.** Melting enthalpy normalized with respect to CL-content as a function of number of CL units in each molecule for the three series of oligomers: T-CLn-B isothermally crystallized (open circles in red) and crystallized during cooling at a rate of 10 K min\(^{-1}\) from the melt (open squares in red), O-CLn-B isothermally crystallized (filled circles in blue) and crystallized during cooling at a rate of 10 K min\(^{-1}\) from the melt (filled squares in blue), and T-CLn-H isothermally crystallized (x in black) and crystallized during cooling at a rate of 10 K min\(^{-1}\) from the melt (crosses in black).

Fig. 16 shows the highest melting points that was possible to achieve for each sample, by crystallizing at the highest isothermal temperatures possible, as a function of reciprocal CL stem length for the oligomers with 4, 8 and 16 repeating units. The melting temperatures of O-CL4-B and O-CL8-B were significantly higher than those of the other 4- and 8-mer oligomers, which was attributed to their double-layer crystal structure. These two data points deviated from the general trend for all the oligomers (line c in Fig. 16).

By shifting these data points to a \(x\)-value corresponding to the effective CL-stem length of the double-layer crystal (shift along the horizontal lines from a to b in Fig. 16) a correlation between melting temperature and reciprocal CL-stem length was obtained. The intercept yielded a value for the equilibrium melting temperature of 357 K. This value is in accordance with data reported by Núñez et al. [53], 357 to 359 K.
It is however also important to factor in that the CL-units did not crystallize to 100 %. The melting enthalpy data for the oligomers with 4 and 8 repeating units suggests that one repeating unit, presumably the unit placed adjacent to the bulky end group, remained in the amorphous state. Furthermore, the crystallinity of the longer oligomers (32 and 64 repeating units) showed an additional depression in crystallinity. These factors were taken into consideration by shifting the melting temperature data along the x-axis by substituting reciprocal full CL-stem length with reciprocal crystalline CL-stem length. The fitted line to this set of data is shown in Fig. 16 (line d, in red). The extrapolated value for an infinite CL crystal thickness was 350 K.

**Fig. 16.** Melting peak temperature as a function of reciprocal CL stem length for the following samples: T-CL\(_n\)-B extended-chain crystals (filled circles in black), T-CL\(_n\)-B folded-chain crystals (open circles in black), O-CL\(_n\)-B extended chain and double-layer crystals (filled squares in blue); the line connects data referring to a single molecule stem length (denoted a) and the length of two CL stems (denoted b), O-CL\(_n\)-B folded chain crystals (open squares in blue), and T-CL\(_n\)-H with extended-chain crystals (filled triangles in red). The straight line (in black) marked c is a linear fit to the experimental data; for O-CL4-B and O-CL8-B only the data points assuming the double-layer CL stem thickness were included in the fitting. The straight line (in red) marked d is a linear fit of the data relating the melting point to the reciprocal crystal CL stem length.
5.4. Chain length and end group influence on molecular packing

By utilizing WAXS data, particularly by looking at the position of the 110 and 200 peaks, it is possible to gain insight into the packing behavior of the samples. High 2-theta values for these peaks correspond to small distances in the unit cell and thus tight packing. Fig. 17 shows data for T-CLn-B oligomers of various lengths that have been crystallized for 5 days at 312 K. The oligomers have packed in a similar unit cell, but small differences can be observed. The lower 2-theta values exhibited by the 8-mer sample suggested that this sample had the least dense unit cell packing amongst the samples. In fact, for all studied temperatures, it could be observed that:

(i) Amongst the T-CLn-B samples the smallest 8-mers exhibited the least dense packing, as packing density increased with increased chain length.
(ii) Amongst the O-CLn-B samples the smallest 8-mers had the most dense packing, as packing density decreased with increased chain length.
(iii) Amongst the T-CLn-H samples the 8-mers had an intermediate packing density, whilst the 16-mers had the highest packing density and the 32-mers had the lowest.

How can these trends be explained? For the T-CLn-B samples the main effect of the bulky t-butyl[dimethylsilyl end group seemed to be that it was difficult to pack in an ordered crystal structure. The shorter the oligomer was, the greater the impact of the end group on overall molecular behavior would be. Thus it should be expected that the least dense packing would be found in the shortest oligomer.

Conversely, amongst the O-CLn-B samples the main effect of end groups was to stabilize a tight crystal structure through hydrogen bonding amongst adjacent hydroxyl groups (and pi-stacking amongst adjacent benzyl groups). The T-CLn-H samples have a bulky t-butyl[dimethylsilyl group at one end and a hydroxyl group at the other end. It was the intermediate 16-mer that fitted in the tightest packing for this combination of end groups, which is explained by the 16-mer having the greatest ability to balance the effect of the two end groups, i.e. potential for hydrogen bonding at one end and bulkiness at the other.
**Fig. 17.** T-CLn-B oligomers of different lengths crystallized for 5 days at 312 K and subsequently quenched, studied with 1.54 Å beam x-ray device. The 110 peaks and the 200 peaks are the two main peaks with value between 20-25 2-theta. The 110 peaks have the lower values of the pair.

**Fig. 18.** T-CLn-H oligomers of different lengths crystallized for 5 days at 312 K and subsequently quenched, studied with 1.54 Å beam x-ray device. The 110 peaks and the 200 peaks are the two main peaks with value between 20-25 2-theta. The 110 peaks have the lower values of the pair.

**Fig. 19.** O-CLn-B oligomers of different lengths crystallized for 5 days at 312 K and subsequently quenched, studied with 1.54 Å beam x-ray device. The 110 peaks and the 200 peaks are the two main peaks with value between 20-25 2-theta. The 110 peaks have the lower values of the pair.
Utilizing WAXS data, it was also possible to compare peaks at lower 2-theta values (see for example the peaks at the left corner of Fig. 17), which represent single layer lamellar ordering of the molecules. Again, clear trends could be observed amongst the oligomers according to end groups. Amongst the T-CLn-B oligomers the peaks at low 2-theta values were much sharper for the 8-mers compared to the longer oligomers (clearly shown in Fig. 17). The same could be noted for the T-CLn-H oligomers, as shown in Fig. 18, but not for the O-CLn-B oligomers as shown in Fig. 19.

The sharp peaks at low 2-theta indicates that packing has occurred in a highly ordered fashion. The smaller 8-mers pack more uniformly than the larger oligomers since the former did not exhibit chain folding and only showed relatively limited chain tilt. The O-CL8-B oligomers seemed to lose some of this ordering, likely since formation of strong hydrogen bonds lead to some loss of uniformity of packing.

5.5. Evolution of molecular packing with time

By studying 2-theta values attained from WAXS analysis it is not only possible to compare chains with different lengths crystallized at the same time and temperature, but also to look at the 110 and the 200 peaks within each system (same sample and temperature) after various crystallisation times. In essence it thus becomes possible to follow the process of crystal packing over time. Before analysis the various monodisperse oligomers were crystallized for between 30 min and 5 days, at different temperatures, followed by quenching.

Intriguingly, it seemed that the oligomers within the first 30 min of crystal formation arranged in stable conformations in which they remained. This was shown by the fact that the positions of the 110 and 200 peaks were virtually identical after 30 min and after 5 days of crystallisation. It could however be observed that peaks were sharper for samples crystallized for longer periods of time, indicating that a greater level of ordering into the same crystal structure occurred during this timeframe. These observations were true for all samples, regardless of end groups, chain length or crystallisation temperature.
In order to capture the initial windows of crystallisation, in situ WAXS experiments from melt were performed. Whilst the molecules were going from melt to isothermal crystallisation with precise temperature control (+/- 0.1 K) WAXS data was collected each 61 s. Temperatures were chosen so as to follow slow processes of crystallisation for the various samples studied. Fig. 20 shows the O-CL8-B sample crystallized from melt at 308 K. It can from the position of the 110 and 200 peaks be concluded that the initial structure formed during the first seconds evolved into a more densely packed structure over the 71 minute time window studied, and that most of the shifts occurred during the first few minutes of crystallisation.

WAXS curves were mathematically fitted in order to separate crystalline peaks from the amorphous background. Successful fits with two amorphous and six crystalline peaks could be performed for all in situ crystallized samples with $s^2$ values typically in the range 0.015-0.02. The fitted curves confirmed that within the first minute or so of crystallisation, samples were organized in crystal structures that did not significantly change in time in terms of peak shifting. The amorphous fractions were however shown to slightly reduce with time, again demonstrating the tendency of the molecules to form a greater level of ordering within the same crystal structure. Polydisperse PCL polymer chains ($M_n = 1000$, without any particular end groups) behaved similarly.

**Fig. 20.** O-CL8-B sample crystallized from melt at 308 K, various times after start of crystallisation, 0.711 Å beam x-ray device. The main peaks to the left are the 110 peaks, whilst the main peaks to the right are the 200 peaks.
5.6. Innate confinement effects and very early phases of crystal formation

In order to further narrow the focus on the very earliest stages of crystal packing, additional in situ WAXS studies were performed using a synchrotron radiation beam. Measurements were taken with only 12s intervals whilst going from melt to isothermal crystallisation, again with exact temperature control. Even higher crystallisation temperatures than before were selected to slow down the process of crystallisation. Fig. 21 shows the O-CL8-B sample crystallizing from melt at 317 K whilst Fig. 22 shows the T-CL16-B oligomer crystallizing from melt at 300 K. Significant repacking arrangements can be observed, particularly for the latter sample:

In the T-CL16-B oligomer the 110 peak compressed from 4.14 Å at 12s to 4.12 Å at 60s, then expanded to 4.19 Å at 72 s, again compressed to 4.14 Å at 96 s and lastly again expanded to 4.18 Å at 300 s. The packing of the 200 peak followed the same trend. The peak compressed from 3.74 Å at 12 s to 3.71 Å at 60 s, expanded to 4.15 Å at 72 s, compressed to 3.74 Å at 96 s and finally expanded to 3.77 Å at 300 s.

The rapid evolution of crystal formation is illustrated by the fact that between 60 and 72s, the packing distance for the 200 peak expanded by fully 12 percent. A comparison of Figs 21 and 22 show that the O-CL8-B sample packed in an ordered structure more rapidly, and with less dramatic shifts, than the T-CL16-B sample. Nevertheless, these two samples had been chosen for detailed analysis since they in previous experiments had shown the greatest shifts occurring during the first min of crystallisation.

Why did these two samples exhibit particularly strong shifts? For the T-CL16-B sample difficulties in packing the bulky t-butyldimethylsilyl end group can explain the early shifts. Similar behavior was observed for T-CL8-B. The O-CL8-B sample likely strived to find a conformation where energetically favorable hydrogen bonding between hydroxyl groups (and pi-stacking amongst adjacent benzyl groups) could be optimized within the scope of the unit cell.
Fig. 21. O-CL8-B sample crystallized from melt at 317 K, various times after start of crystallisation, 0.908 Å beam x-ray device. The main peaks to the left are the 110 peaks, whilst the main peaks to the right are the 200 peaks.

Fig. 22. T-CL16-B sample crystallized from melt at 300 K, various times after start of crystallisation, 0.908 Å beam x-ray device. The main peaks to the left are the 110 peaks, whilst the main peaks to the right are the 200 peaks.

Early crystalline structures, with an ephemeral nature did indeed exist during the early crystal formation. In addition, the innate confinement effects created by the bulky t-butyldimethylsilyl, but also the potential of hydrogen bonding, led to a more pronounced role for early structures compared to in other samples.

5.7. Unit cell determination

A detailed unit cell was determined for a T-CL8-H sample which had been crystallized for 5 days at 312 K. WAXS data of the sample featured nine peaks which were dependent on one very long cell dimension. The ten remaining peaks could be indexed by a tetragonal unit cell.
The cell dimensions were \( a = b = 6.34 \, \text{Å} \) and \( c = 83.04 \, \text{Å} \), with \( c \) being the long cell dimension representing the entire length of the packed molecule. The unit cell volume was \( 3337 \, \text{Å}^3 \). The cell seemed to contain 4 oligomer molecules showing four-fold symmetry as expected from all possible tetragonal space groups.

As a comparison Chatani et al. reported in 1970 that linear PCL polymers (without special end groups) packed in an orthorhombic unit cell with the parameters \( a = 7.47 \, \text{Å}, b = 4.98 \, \text{Å} \) and \( c = 17.05 \, \text{Å} \) [68]. The same year Bittiger et al. [65] reported an identical space group with essentially the same packing (but with a planar zig-zag conformation), concluding that the unit cell parameters were \( a = 7.50 \, \text{Å}, b = 4.97 \, \text{Å} \) and \( c = 17.30 \, \text{Å} \).

### 5.8. Data modeling results

Computer modelling experiments were performed in order to gain greater insight into how molecular packing behaviour could be affected by the various end groups. These experiments supported experimental findings that it is difficult to fit the bulky \( t \)-butyldimethylsilyl groups in orderly structures. Modelling studies showed that molecules can adopt three different strategies to pack bulky end groups during energy minimization.

The first two strategies are shown in Fig. 23 and 24 for a model where 16 T-CL8-B oligomers were initially placed in slightly disordered, bended, alignment. All molecules had the same alignment, i.e. were not placed according to the zig-zag unit cell, at the start of the experiment. This packing was chosen to have the molecules less locked in the starting condition compared to when placed in a tightly packed zig-zag unit cell conformation.

**Strategy 1:** The bulky end \( t \)-butyldimethylysilyl end groups move to the vacant spaces in the model. This behaviour can clearly be seen in Fig. 23, where both images are taken after energy minimization. The left image shows the end where the \( t \)-butyldimethylysilyl end groups are placed and the right image shows the end where the benzyl end groups are placed. The former end groups have clearly spread out during energy minimization to the vacant spaces in the model compared to both the CL backbone chains and also the benzyl groups.
**Strategy 2:** The CL chains move closer together during the minimization step, which can be seen in Fig. 24, where the left image shows the model before and the right image shows the model after energy minimization. During the process the chains have maximized their energy by shifting along their c-axis, so that their t-butyldimethylsilyl end groups do not lie directly on top of each other. Shifting leads to overall less energetically favourable interaction between backbone CL chains but diminishes tension from having bulky end groups too close to each other.

Note in Fig. 24 that already when placing the molecules in the starting positions, it was important to align the molecules so that their end groups were not on top of each other, as such an conformation was almost impossible to arrange. Note also how this form of shifting at one end could impede formation of hydrogen ends on the other end, which explains why the presence of t-butyldimethylsilyl groups on one end of the molecule could impede hydrogen bonding at the other end for the T-CLn-H samples.

**Fig. 23.** ChemBio3D Ultra modelling of 16 T-CL8-B samples after energy minimization. The molecules were placed in a disordered bended alignment before undergoing energy minimization. The left image shows the end of the molecule where the t-butyldimethylsilyl end groups are places whilst the right image shows the end where the benzyl end groups are placed.
Strategy 3: The PCL chains do not pack in a conformation where all (or most) “A” end groups are placed on one end of the crystal lamellae and all (or most) “B” end groups are placed at the opposite end, but rather in a conformation where each A end group is surrounded by B end groups and vice versa. This strategy was shown to be more energetically favourable for T-CLn-B and T-CLn-H oligomers containing the t-butyldimethylsilyl end groups, since it is easier to fit half of the bulky groups at one end and the other half on the other end of the structure.

The strategy of packing all A end groups at one side and all B end groups at the other was on the other hand more energetically favourable for the O-CLn-B oligomers, which did not contain the bulky end groups and could form hydrogen bonds. The O-CLn-B oligomers benefitted from a structure where hydroxyl groups were focused at one end and could form hydrogen bonds with each other, whilst pi-stacking between benzyl groups could occur at the other end. Such interactions were not as beneficial for the T-CLn-B (which could form pi-stacking amongst benzyl groups) and T-CLn-H (which could form hydrogen bonding at hydroxyl groups) since presence of bulky t-butyldimethylsilyl groups at one end limited the potential for energetically favorable interactions at the other end.

It is likely that strategy 2 and 3 are the main strategies which the molecules rely on in reality. Strategy 1 is not viable in the real world since, contrary to in the computer model, there is no (or very limited) “empty space” which the end groups can move into.
5.9. Crystallisation of linear chains in nano-sized pores

As discussed in previous sections, the innate confinement effects arising due to presence of the bulky t-butyldimethylsilyl end groups did indeed result in confined crystallisation. The second strategy for achieving confinement was to crystallize PCL chains in systems containing nanopores of various sizes. It was observed that the polymer chains preferentially entered the pores, rather than interacting with the CPG surfaces, and also that the ability of the polymers to form stable crystals was strongly affected by pore dimensions.

In order to gain insight into the progression of crystal formation was studied in the different pore systems. Figs. 25 and 26 show the crystallisation progress of linear PCL chains with $M_n = 10\,000$ in pristine systems, in various nano-porous systems (CPG1-5) and in the presence of non-porous glass beads (NPG) used as a reference (properties shown in table 3). All samples were crystallised at 312 K at different times.

The crystallisation progress was strongly inhibited in the CPG1 systems (with 10 nm pores) which only reached a crystallisation degree of ca 4 % after 15 min of isothermal crystallisation, compared with 81-94 % in the systems with pore sizes ranging from 23-294 nm (CPG2-5). The stark difference between the 10 nm and the 23 nm pore systems is a remarkable proof of how a small change in pore dimension can affect the ability to form stable crystalline structures.

Crystallisation kinetics depended strongly on not only pore size but also chain length. Figs. 27 and 28 shows the crystallisation of a linear PCL chain with $M_n = 42\,500$ whilst Figs. 29 and 30 shows the data for an even longer chain with $M_n = 80\,000$. Also the latter data are collected from experiments carried out at a crystallisation temperature of 312 K.

For the intermediate chain with $M_n = 42\,500$ crystallisation in the CPG2-5 systems with pore sizes 23-294 nm pores occurred similarly to but more rapidly than for the pristine polymer samples, as interaction with the particles initiated crystal growth formation. As shown in Fig. 27, the CPG1 system with 10 nm pores on the other hand crystallised very slowly, reaching a crystallisation progress below 2 % after 15 min whereas the systems with larger pores reached a crystallisation degree of 74-89 %.
**Fig. 25.** Heat of fusion for PCL-10 samples crystallised at 312 K for various times. Data shown for CPG1-CPG4 systems.

**Fig. 26.** Heat of fusion for PCL-10 samples crystallised at 312 K for various times. Data shown for CPG5, NPG and pristine systems.
**Fig. 27.** Heat of fusion for PCL-43 samples crystallised at 312 K for various times. Data shown for CPG1-CPG4 systems.

**Fig. 28.** Heat of fusion for PCL-43 samples crystallised at 312 K for various times. Data shown for CPG5, NPG and pristine systems.
Similarly, the $M_n = 80\ 000$ chain crystallised more rapidly in the CPG3-5 systems with pore sizes 53-294 nm compared to in pristine form. Also this longer chain crystallised more slowly in the CPG1 system with the smallest pore sizes. However, contrary to the two shorter chains for this longer chain a clear confinement effect could also be observed for the CPG2 system with the second smallest pore sizes. As shown in Fig. 29 the $M_n = 80\ 000$ polymer chain reached a crystallisation degree of under 2% in the 10 nm pore system after 15 min, compared to 65% in the 23 nm pore system and 74-94% in the 35-294 nm pore systems.

Since crystallisation occurred slowly for the various chains crystallised in CPG1 systems with 10 nm pore diameter, crystallisation times up to 120 min were run for these samples. The results of these experiments are shown in Fig. 31. The shortest chain, with $M_n = 10\ 000$, reached a crystallisation progress of 27% after 120 min compared to 22% for the intermediate chain with $M_n = 42\ 500$ and 19% for the longest $M_n = 80\ 000$ chain. Clearly the molecules experience a strong confinement effect, which was affected by both the length of the chains and the diameter of the pores.

![Fig. 29. Heat of fusion for PCL-80 samples crystallised at 312 K for various times. Data shown for CPG1-CPG4 systems.](image-url)
Fig. 30. Heat of fusion for PCL-80 samples crystallised at 312 K for various times. Data shown for CPG5, NPG and pristine systems.

Fig. 31. Heat of fusion for CPG1 systems crystallised at 312 K for various times. PCL1 stands for 10 000 Da molecular size, PCL2 stands for 42 500 Da molecular size whilst PCL3 stands for 80 000 molecular size.
5.10. Crystallisation of star-shaped polymers in small pores

When crystallizing a star-shaped CL oligomer, with four arms of approximate $M_n = 1\,000$ each, confinement effects were more pronounced compared to when crystallizing the linear chains. Fig. 32 shows the crystallisation progress of the star-branched sample at 312 K in the same CPG, NPG and pristine systems as previously utilized for linear chains. Given enough time (300 h), the star-branched polymer reached a crystallisation degree of above 80% in all systems, but the kinetics were considerably slower for the systems with the smallest pores.

For the linear polymers discussed in the previous section, crystallisation had been impaired only in the 10 nm pore system for chains of $M_n = 10\,000$ and 42\,500 and only in the 10 and 23 nm pore systems for chains of $M_n = 80\,000$. For the star-shaped polymer however, a pore size effect could be observed for all CPG systems, as shown in Fig. 32. It can readily be observed that the pristine system experienced the fastest crystal formation, followed by the slightly confined CPG5 system, the more confined CPG3 system and finally the most confined CPG1 system. The CPG4 and CPG2 systems followed the same trend, but are excluded from Fig. 32 for sake of clarity.

![Fig. 32. Heat of fusion for star-branched PCL oligomer crystallised at 312 K for various times.](image)

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It is worth noting that this is explained mainly by differences in molecular architecture rather than size. The star-shaped oligomer has only a molecular size of 4270 Da, compared to 10-80 kDa for the three linear chains. A more important factor than the molecular size is the radius of gyration.

The radius of gyration $R_{g,PCL}$ of the linear chains can be estimated from $R_{g,PCL} = b \times M_n^{1/2}$, with $b = 0.031$ as calculated from reported data of intrinsic viscosity under theta conditions [69-71]. Under the assumption of theta solvent, values of $R_{g,PCL}$ were estimated to 3.1 nm for PCL-10, 6.4 nm for PCL-43 and 8.8 nm for PCL-80. For uniform star-shaped molecules having f-arms with no long range intramolecular interaction an analytical solution has been developed by Zimm and Stockmayer [72] for calculating relative size where $g(f) = \frac{3f^{2} - 2}{f^{2}} = 0.625$ for a four-armed chain. Utilizing both equations the $R_{g,PCL}$ can be estimated to 1.3 nm for the STAR-4000 chain with molecular mass 4270 Da.

The difference in $R_{g,PCL}$ is thus more significant between the star-branched oligomer and the linear chains than the difference in molecular weight. But although the STAR-4000 has a significantly smaller $R_{g,PCL}$ it is more profoundly affected by confinement. How can this be explained? The explanation lies in the difficulty to pack all four arms in an orderly crystal. The crystallizing elements in the star-shaped oligomer are fixed, creating an innate confinement effect on crystallisation which seems to make the STAR-4000 more sensitive to physical confinement than longer linear chains.

5.11. Trade-off between mobility and initiation sites

When studying the star-branched oligomer it is clear that it was affected by two opposing trends, both arising due to confinement. The two trends can be distinguished by comparing crystallisation at different temperatures. Figs 33 and 34 show isothermal crystallisation of STAR-4000-impregnated systems at 310 and 300 K respectively. When crystallising at 310 K the smallest CPG1 system crystallises most slowly, whilst the pristine system crystallises most rapidly, in line with observations of crystallisation at 312 K.
However, although the intermediate CPG3 system initially crystallises more slowly than the largest CPG5 system, the former system eventually catches up and even surpasses the latter. A stark clear can be observed by lowering the crystallisation temperature only 2 degrees. When crystallising at 300 K even more remarkable differences could be observed. Also at this temperature the smallest CPG1 system crystallises most slowly. However, the intermediate CPG3 system rapidly surpassed not only the CPG5 but also the pristine system in terms of crystallinity.

Why did the systems with the larger pores exhibit the fastest crystallisation kinetics for the star-shaped oligomer at the very beginning and at high temperatures? The logical reason seems to be greater mobility. Particularly when the temperature, and thus chain movement, was high, the star-shaped molecules found it challenging to pack all arms in an ordered crystal structure within the confinement of small pores. This effect was mainly important in the beginning, as interaction with existing crystal structure which could facilitate crystallisation were non-existent or limited for each individual chain.

![Graph](image)

**Fig. 33.** Heat of fusion for star-bransched PCL oligomer crystallised at 310K for various times.
**Fig. 34.** Heat of fusion for star-branched PCL oligomer crystallised at 300K for various times.

Why did smaller pore sizes benefit crystallisation kinetics at lower temperatures and during later stages of crystal formation? The likely reason is that smaller pore sizes translated into more sites for initiation of crystal formation. When temperature, and chain movement, was lower this effect could dominate.

The challenge of finding a good way of folding the four arms in a stable crystalline form was initially easier overcome in systems with high mobility. Once some chains had folded however, they could facilitate folding of other chains. This interaction was greatest in the smaller pore systems, where the polymer molecules were more likely to interact with each other given the confined environment. Therefore the effect of pore size was not the same during early and later stages of crystal formation.

For the CPG1 system, the size confinement so strongly inhibited mobility that crystallisation always occurred more slowly than in the other systems. For all other CPG systems, there was a trade-off in terms of which system benefited more from the two counteracting phenomenon of mobility and initiation sites, depending on temperature and whether we look at early or late stages of crystal formation.
5.12. Hitherto unreported rectangular crystals created by RESS process

The studies focusing on innate confinement effects and confinement in nanoporous environments were based on calorimetric measurements. The studies where RESS and Inkjet technologies were utilized however aimed at confining the ability for crystal growth through spraying techniques. The thin films that were formed were mainly examined in terms of morphology to examine single crystal shapes.

Deposition of PCL dissolved in supercritical CO$_2$ and 0.1 vol.% chloroform resulted in a rapid temperature drop, due to the very rapid phase transition from a supercritical to a gas-like state. The temperature momentarily fell to below 220 K at the silica surface where the material was deposited, which is in agreement with results presented by Werner and Turner [73]. On the surface six-sided crystals, shown in previous studies to be formed by PCL, were only sparsely observed.

A more common structure observed in our work was flat single crystals with more irregular angles. The crystals had angles and shapes that were close to, but not identical to those exhibited by six-sided PCL crystals found in previous studies. A large variation was found in shapes and angles of the more irregular crystals, some of which are shown in Fig. 35 (indicated by white arrows). The results indicate that transient structures, not observed by other deposition techniques, were "frozen-in" place. Another commonly found structure was the remarkable rectangular crystals, which have hitherto not been reported for PCL. Fig. 36 displays images of these crystals.

The crystals varied in size, and had angles that were in the range 90 ± 15°. Hot-stage AFM studies were performed in order to gather further information on these unique crystal structures. Fig. 37 shows the effect of on heating on two single PCL crystals of rectangular shape. The two objects of study were a large 27 nm thick rectangular crystal (included the crystal and two amorphous layers; it is possible that this structure in fact consisted of two stacked crystals) present in the center of the image and a smaller 11 nm thick rectangular crystal present at the bottom left-hand side of the image.
**Fig. 35.** Height AFM image of deposited crystals showing irregular groups of crystals and flat (single crystal-like) crystals; the latter being indicated by arrows.

**Fig. 36.** Height AFM images of rectangular crystals (a) with close up (b, c).
No morphological changes were revealed on heating the sample to 30 °C or during the 30 min isothermal period (still at 30 °C). After heating to 35 °C and 30 min rest at this temperature subtle changes (formation of niches) at the edges of the two crystals occurred (indicated by arrow in the micrograph). Further heating and resting at 40 °C caused further rearrangements at the crystal edges of the crystals. The shape of the crystal changed from the original rectangular to a crystal with new facets with other angles between adjacent facets. In addition some internal modification of the crystal at 40 °C was observed (indicated by black arrows). The thicknesses of the two rectangular crystals decreased on heating to 40 °C: from 27 nm to 23 nm for the large crystal and from 11 nm to 6 nm for the small crystal. At 45 °C both crystals had melted. A ca. 1 nm thick trace of both crystals could however still be observed. It can be noted that the two crystals melted in the same temperature range, although their initial heights differed almost by a factor of two.

**Fig. 37.** Height AFM images of a rectangular crystal at the following temperatures: (a) 20 °C, (b) 35 °C, (c) 40 °C, (d) 45 °C. White arrows indicate sites of initial melting along the crystal edges, whereas the black arrows indicate small regions that have retained a high crystal thickness at 40 °C.
As a comparison, Fig. 38 shows the thermally induced changes in a 10 nm thick crystal with irregular shape. No morphological changes were observed at either 30 or 35 °C. The periphery of the crystal remained intact even after heating to 45 °C, but some internal changes was visible (indicated by the black arrows). Further heating reaching 50 °C caused further internal changes (also indicated by black arrows) and also more subtle changes at the edges (indicated by white arrows). The crystal was fully melted at 55 ºC (not shown).

Fig. 38. Height AFM image of an irregular crystal at the following temperatures: (a) 20 °C, (b) 35 °C, (c) 45 °C, (d) 50 °C. White arrows indicate sites of initial melting along the crystal edges, whereas the black arrows indicate small regions where morphological changes occur in the central regions of the crystal.

Núñez et al. [55] have previously studied melting of solution grown PCL single crystals and have shown that no morphological changes were revealed at temperatures below 55 ºC for a 9 nm thick crystals. Melting occurred between 55 and 60 ºC. This is in line with observations by Mareau and Prud'homme [51] of film-grown PCL crystals. Both observations were made for the traditional six-sided single crystals typically formed by PCL. The rectangular crystals in this work, however, melted completely between 40 and 45 ºC. The melting temperature
was thus 10 to 15 ºC lower than that previously reported for solution-grown single crystals of PCL. The irregular crystal of similar systems melted between 50 and 55 ºC, which is still slightly lower than that previously reported but higher than for the rectangular crystals.

5.13. Two sets of scattering peaks created by RESS process

The PCL film created by the RESS technique was analysed through WAXS and compared to WAXS data based on crystallising PCL from melt. When crystallising from melt, the well-known orthorhombic phase gives rise to two main peaks, a 110 peak representing a molecular packing distance of 4.1 Å and a 200 peak representing a molecular packing distance of 3.7 Å. The RESS process however gives rise to a more complicated structure, as shown in Figs. 39 and 40. Data indicated that at least two different phases existed on the surface with similar crystal structure but adopting two different lattice constant due to potentially different confinement. The X-ray scattering patterns taken indicated a polymorphic structure also including the 110 and 200 peaks. Several different c-axis repeating distances were observed ranging from 3.7 to 4.7 nm. The equatorial diffraction peaks were numerous and mainly placed on lower $Q$-values than the orthorhombic main diffraction peaks. This indicates longer lateral periodic distances and a less dense packing of the PCL stems.
Fig. 39. A typical two-dimensional image of X-ray scattering pattern taken at SDD 197.08 mm. The two areas marked by red dashed line are the integration regions for low and high Q-diffraction peaks, used for calculating values in Fig. 39.
Fig. 39. Sketch of unit cell structure of PCL and the direction of the lateral faces, (110) and (100). The mature crystal structure according to Hu and Dorset [15] is displayed in grey and the lateral faces are in red. The angles between the faces are shown in red. An expansion of the unit cell along \( b \) is displayed in blue and the new angles between the crystal faces are displayed also in blue. The expansion of the cell along \( b \) is ca. 2 Å.
5.14. Single crystals confined in growth by small droplets and low concentration

Deposition of single droplets through the Inkjet technique resulted in different conditions for the growing crystals compared to when deposing by the RESS technique. In the latter case, rapid evaporation (due to small droplets and phase transition of the main solvent) and significant temperature drop occurred. In the former case, evaporation was rapid (due to the small droplets) but deposition occurred at room temperature. The Inkjet technique however allowed for very precise control of both droplet size and polymer concentration.

Fig 41 shows structures formed after deposition of single 110 pikolitre sized droplets of $10^{-6}$ gl$^{-1}$ PCL solution (10 000 Da molecular weight). Very small structures could be observed, trapped in a metastable state as they were hindered from growing by the lack of polymer material in their vicinity. The smallest structures had diameters of ca. 20 nm whereas the largest ones had diameters of ca. 60 nm (translating to 10 nm and 50 nm respectively, when the effect of the AFM tip with 5 nm radius is taken into account). The smallest structures were only ca. 2 nm high, compared to the largest structures that had a height of 10 to 11 nm. These structures were interpreted as precursors to the six-sided single crystals previously observed for PCL. Some of the facet angles found were close to the theoretical angles of the mature six-sided crystals, i.e. 113° (angle between the {110} and {110} sectors) and 124° (angle between the {110} and {100} sectors).

In addition, small structures with a rectangular shape were observed. The insert in Fig. 42 shows part of a structure formed after deposition of 10 droplets of $10^{-6}$ gl$^{-1}$ PCL solution. Interestingly, the image shows features with a rectangular shape (marked by the white outline). These rectangular shapes seem to represent a similar structure as when depositing PCL through the RESS process.

It is very interesting to note that both techniques aimed at confining the ability of crystal growth through unusual methods of deposing PCL on surfaces led to the observation of the hitherto unreported rectangular PCL single crystals. The rectangular shaped structures were quite uncommon when depositing through the Inkjet technique, whereas they were one of the main species of single crystals observed on the surfaces deposited by the RESS technique.
**Fig. 41.** Height AFM image of structures formed after deposition of a single droplet of $10^6$ gL$^{-1}$ PCL solution.

**Fig. 42.** Height AFM image of structures formed after deposition of 10 droplets of $10^6$ gL$^{-1}$ PCL solution. The insert image shows a close up of region marked with a dashed outline in the right-hand image.
6. Conclusions

The various strategies utilized to confine crystallisation all impacted crystalline features significantly. Innate confinement effects arising from the presence of bulky end groups did indeed influence crystal formation amongst CL oligomers. Oligomer chains forced to deal with the difficulty of packing bulky end groups at one end were inhibited from forming strong hydrogen bonds at their other ends. Hydrogen-bonding end groups promoted the formation of crystal bilayers. The longer chains with 32 and 64 repeating units could not unfold and form crystals with fewer folds or extended chains even at the high-temperature limit of crystallisation where crystallisation occurred over hundreds of hours. The interaction between end groups and end groups, as well as that between end groups and CL repeating units, created an obstacle for unfolding the crystal structures that had initially formed. Innate effects thus confined crystal formation in more than one way. Very rapid x-ray imaging of the in situ crystallisation process, performed at high temperatures where crystals formed slowly, showed that rapid shifts in the unit cell occurred during the first minute of crystallisation due to the difficulty of fitting the bulky end groups in a stable unit cell.

Confinement effects also arose when polymer chains were crystallized in systems with small pore sizes. Linear polymers with \( M_n = 10\ 000 \) and \( 42\ 500 \) were strongly inhibited from forming crystal structures in 10 nm pore systems, but not hindered in 23 nm pore systems. Longer chains with \( M_n = 80\ 000 \) were strongly hindered in the 10 nm systems, but also somewhat in the 23 nm systems. A star-shaped oligomer with four arms of approximately \( M_n = 1\ 000 \) each was most strongly affected by pore size as it was inhibited from forming crystal structures even in larger pores. The challenge of packing all four arms in an orderly crystal structure clearly increased the importance of physical confinement. The confinement effect depended on the dimensionality of the pores as well as that of the polymer samples. For the star-shaped oligomer, a trade-off existed between mobility and number of sites for initiation of crystallisation. At high temperatures and during early stages of crystal formation crystallisation occurred more rapidly in the larger pores and in pristine samples where mobility was high, allowing greater freedom for the four arms to pack in an orderly fashion even when interaction with existing crystal structure which could facilitate packing was non-existent or limited for each individual chain. At lower temperatures and during later stages of crystal formation, however, crystallisation could in fact occur faster in smaller pore systems,
which offered more sites for initiation of crystal formation. The innate confinement effect created by the challenge of packing four arms was thus shown to have strong temperature dependence.

The two last strategies of confining crystal growth were based on unusual ways of deposing linear chains on silicon substrates. The RESS technique led to a very rapid temperature drop as well as rapid evaporation of the supercritical solvent. Hitherto unreported rectangular crystals could be observed when deposing PCL through this method, as well as six-sided crystals previously observed. The rectangular crystals seemed to have formed in metastable unit cells with different characteristics than previously reported for PCL. The structures melted in considerably lower temperature range than the six-sided crystals created by the same method and even lower temperatures compared to six-sided crystals observed in previous work. The Inkjet technique involved disposition at room temperature. The very precise deposition of small droplets with very low concentrations allowed for two mechanisms of confining crystal growth: rapid evaporation of small droplets which reduced the time window for crystal growth and limitations to the size of the microcrystals by the lack of polymer material in their vicinity. By utilizing this method, previously not used for in-depth crystallisation work, minute crystal structures could be observed. Also in this work rectangular crystal structures could be observed, likely formed due to entrapment in metastable phases since the crystals were confined in their growth.
7. Suggestions for future work

Previous studies dealing with confinement have mainly dealt with physical confinement in small pores, although limited attention has been given to how the crystallisation kinetics is affected. This work has focused on how physical confinement affects crystallisation kinetics as well as attributes such as melting temperature and crystalline structure. In addition, strategies of confining crystal growth by innate effects as well as by utilizing unique spraying techniques have been employed. The broad focus on how confinement can be achieved differs from much of the work done in the field.

Perhaps the most interesting way of continuing the present studies would be to examine how different strategies for achieving confinement can affect each other. In this work it could be observed that star-branched oligomers were more significantly affected by physical confinement compared to linear chains, likely since the star-branched molecules also had to deal with innate confinement effects. One form of confinement seems to reinforce another. Building upon this notion, it would be interesting to study what would happen if polymers with innate confinement effects (such as bulky end groups and/or star-shaped forms) were deposited through the RESS or Inkjet techniques?

Furthermore, it would be highly interesting to continue working on the hitherto unreported rectangular PCL single crystals found by the RESS and Inkjet techniques, which differ from the six-sided single crystals previously observed for PCL. Do other polymers deposited in the same fashion also form unique structures due to confinement in metastable phases?

Lastly, the work on utilizing the Inkjet method for studying small crystal structures deserves to continue. By using smaller nozzles and more dilute solutions, even smaller droplets can be deposited which contain on average only a single polymer chain. Indeed, Inkjet printing can be used to create whole surfaces consisting of single polymer chains deposited in rapidly evaporating droplets, where the individual chains are deposited in proximity to each other but have no direct contact.

By creating and studying such surfaces, much knowledge could be gained on the process of crystallisation in confined systems. This would in turn further our understanding of the
process of crystallisation as a whole. It is worth emphasising that systems where a small number of oligomers form nano-scale structures are not only interesting to study in order to gain insight into early metastable phases, but also since similar systems will likely become more and more useful as nanotechnology applications develop.
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