Supplementary Information

1. General Methods
2. Monomer Synthesis
3. Polymer Synthesis
4. Analysis of FT-IR Data
5. Detailed analysis of the SAXS of P44/5-Prop
6. Details on the morphology of P44/5
1. General Methods

Solution $^1$H-NMR (Nuclear Magnetic Resonance) spectra were obtained using 200 and 300 MHz Varian Gemini, and 300 and 500 MHz Bruker spectrometers. High-temperature size exclusion chromatography analysis were performed by CERTECH (Seneffe, Belgium) on a Waters ALC/GPC 150C instrument, using one Showa Denko AT-800 P Shodex precolumn, two Showa Denko AT-806 MS Shodex columns, and one Waters HT 2 column. Samples were first dissolved at 160°C during 1 hour in 1,2,4-trichlorobenzene (TCB) stabilized with BHT (1 g.l$^{-1}$). 120 µl were injected and eluted (135°C, 0.8 ml.min$^{-1}$) in the same solvent. A differential refractometer (DRI) was used for detection. The data were treated using the Millenium 32 Chromatography Manager from the Waters Company, based on the universal calibration protocol. A polystyrene-specific calibration was established from narrow polystyrene standards and transformed into a polyethylene-specific calibration curve using the Mark-Houwink equations for both PE and PS:

\[
[\eta] = 1.21 \times 10^{-4} M^{0.71} \quad \text{(polystyrene)}
\]

\[
[\eta] = 5.10 \times 10^{-4} M^{0.706} \quad \text{(polyethylene)}
\]

where $[\eta]$ is the intrinsic viscosity, and $M$ is the molar mass of the polymer.

Elemental analyses were obtained from the University College London Analytical Services and the Microanalysis Laboratory at the University of Massachusetts. FTIR (Fourier Transform Infra-Red) spectra of the polymers were obtained from Perkin Elmer 1710, BioRad FTS 135 and Bruker IFS55 spectrometers on KBr pellets or pressed polymer films obtained by
compressing a molten sample for one minute, then cooling down to room
temperature. DSC 7 Perkin-Elmer Differential Scanning Calorimeter (DSC)
equipped with a controlled cooling accessory (CCA7) and Pyris DSC 1 Perkin-
Elmer calorimeter equipped with a cryofill liquid nitrogen cooling system were
used to investigate the polymer melting behavior. The instruments were
calibrated with indium and zinc (DSC 7) or with indium and eicosane (DSC 1).
Measurements were obtained at 10 K.min⁻¹ in aluminum pans.
2. Monomer Synthesis

Commercially available 3-\textit{n}-propyl-glutaric acid (Lancaster) and thionyl chloride (Acros) were purchased and used without further purification.

\textbf{3-\textit{n}-Propylglutaryl dichloride.} 1.89 g (1.085.10^{-2}\text{mol}) of 3-\textit{n}-propyl-glutaric acid was slowly added to 9.06 g (7.615.10^{-2}\text{mol}) of thionyl chloride. After 1.2 h, the mixture was maintained for 49.2 h at 45-50°C. The excess thionyl chloride was removed under reduced pressure and the product was fractionated at 0.96 mbar to yield 1.75 g (8.29.10^{-3}\text{mol}, 76\%) of 3-\textit{n}-propylglutaryl dichloride as a colorless liquid. B.p. 83°C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200MHz, RT): \(\delta\) (ppm) 2.99 (4H, -CH\textsubscript{2}-\textit{C}(=O)-, d, 6.4 Hz), 2.46 (1H, CH-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{3}, m), 1.2-1.5 (4H, CH-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{3}, m), 0.92 (3H, CH-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{3}, t, 7 Hz).

\textbf{\textalpha,\textomega-Alkanediols.} The synthesis of 1,22-docosanediol (C\textsubscript{22} diol, HO-(CH\textsubscript{2})\textsubscript{22}-OH) and 1,44-tetratetracontanediol (C\textsubscript{44} diol, HO-(CH\textsubscript{2})\textsubscript{44}-OH) is described elsewhere.\textsuperscript{1} 1,12-Dodecanediol (C\textsubscript{12} diol, HO-(CH\textsubscript{2})\textsubscript{12}-OH) was purchased from Janssen Chimica.
3. Polymer Synthesis

1,22-Docosanediol and 1,44-tetratetracontanediol were dried under vacuum before use. o-Dichlorobenzene (Fluka, Aldrich) was dried by refluxing over CaH₂ and stored over 4 Å molecular sieves. Methanol (Riedel-deHaën, Mallinckrodt) was used without further purification. The synthesis of the linear poly(alkanediol-alt-glutaric acid) polyesters P22/5 and P44/5 is reported elsewhere.¹

**Poly(1,22-docosanediol-alt-3-n-propyl-glutaric) P22/5-Prop.** 1,22-Docosanediol (0.259 g, 0.21 mmol) and 2.1 mL of o-dichlorobenzene were added to 0.160 g (0.76 mmol) of 3-n-propylglutaryl dichloride in a polymerization tube capped with a CaCl₂ drying tube and a NaOH/H₂O trap. The tube was immersed in an oil bath at 70°C. After 0.4 hours of reaction, a gentle stream of argon was introduced into the solution in order to facilitate removal of the hydrochloric acid formed during the reaction. The polyester obtained after 2.7 h was precipitated in cold methanol under stirring, yielding 300 mg (82% yield) of a white solid after filtration and vacuum drying.¹¹H NMR (CDCl₃, 200MHz, RT): δ (ppm) 4.06 (4H, -C₆H₄-O, t, 6.55 Hz), 2.34 (5H, -C(=O)-C₆H₂-C₆H₂-C₆H₂ and -C₆H₂-, m), 1.6 (4H, -C₆H₂-O-, m), 1.2 (40H, CH-C₆H₂-C₆H₂-C₆H₂ and -C₆H₂-, m), 0.89 (3H, CH-C₆H₂-C₆H₂-C₆H₂, m). Elemental Analysis: (C₃₀H₅₆O₄)n. Calcd.: C, 74.95; H, 11.74. Found: C, 74.62; H, 11.61. FTIR (KBr pellet): 3447, 2918, 2850, 1735, 1466, 1395, 1317, 1175, 721 cm⁻¹. FTIR (polymer film): 2917, 2851, 1735, 1468, 1417, 1395, 1369, 1104, 1072, 996, 925, 739, 720 cm⁻¹. SEC
Poly(1,44-tetratetracontanediol-alt-3-n-propylglutaric acid) P44/5-Prop.

0.136 g (0.21 mmol) of 1,44-tetratetracontanediol and 1.00 mL of dried o-dichlorobenzene were added to 0.0445 g (0.21 mmol) of 3-n-propylglutaral dichloride in a polymerization tube capped with a CaCl$_2$ drying tube and a NaOH/H$_2$O trap. The tube was immersed in an oil bath at 85 °C. After 2.4 hours of reaction, a gentle stream of argon was introduced into the solution in order to facilitate removal of the hydrochloric acid formed during the reaction. The polyester obtained after 43 h was precipitated from the hot solution in 20 mL of methanol under stirring. The resulting solid was filtrated and dried under vacuum, yielding 155 mg (94% yield) of a white, low molecular-weight solid (SEC (PE equivalent, Dalton): $M_n$ 9.3 x 10$^3$, $M_w/M_n$ 1.5). A post-polymerization (chain-extension) was performed on 108 mg of the polymer with a seven-molar excess of diacid chloride in 0.11 mL of o-dichlorobenzene for 4.4 days. An off-white solid was obtained after precipitation of the hot solution in 13 mL of methanol, filtration and drying. $^1$H NMR ($C_6D_4Cl_2$, 500MHz, 80°C): $\delta$ (ppm) 4.30 (4H, -CH$_2$-O-, t, 6.5 Hz), 2.5-2.7 (5H, -C(=O)-CH$_2$-CH($\text{-CH}_2\text{-CH}_2\text{-CH}_3$)-CH$_2$- C(=O)-, m), 1.8-1.9 (4H, -CH$_2$-CH$_2$-O-, m), 1.4-1.8 (84H, CH-CH$_2$-CH$_2$-CH$_3$ and -(CH$_2$)$_{40}$-, m), 1.09 (3H, CH-CH$_2$-CH$_2$-CH$_3$, t, 6.4 Hz). Elemental Analysis: (C$_{52}$H$_{100}$O$_4$)$_n$. Calcd.: C, 79.12; H, 12.77. Found: C, 78.29; H, 13.03. FTIR (KBr pellet): 2918, 2850, 1736, 1637, 1617, 1473, 1464, 1178, 730, 719, 620, 473 cm$^{-1}$ (720-730 cm$^{-1}$ splitting observed on polymer fibers). SEC (PE equivalent, Dalton): $M_n$ 8.6 x 10$^3$, $M_w/M_n$ 2.70. TGA decomposition temperature: 380°C.
4. Analysis of FT-IR Data

Infrared spectra were used to confirm the adoption of the O⊥ crystal packing by the polymers. Polyethylene² and orthorhombically crystallised linear alkanes³ show two splittings of infrared-active modes at 720-730 cm⁻¹ (ρ CH₂ in-plane bending or rocking vibration mode)⁴ and 1462-1473 cm⁻¹ (δ₉ CH₂ in-plane bending or scissoring vibration mode)⁴, respectively. These correlation field splittings (sometimes referred to as “Davydov” or “factor group splittings”) originate from intermolecular interactions in the solid state⁵. In the present case, they are characteristic of orthorhombic crystals and originate from the two possible changes in dipole moment in each mode, a consequence from the movements of the four hydrogen atoms of the two chains in the orthorhombic crystal cell.
5. Detailed analysis of the SAXS of P44/5-Prop

2.1. Fitting Procedure. The structure shown in Fig. S1 for the lamellae, with a core of electron density $\rho_1$ corresponding to the crystallised aliphatic region of thickness $z_1$, bordered by regions of different electron density (thickness $z_2$ and electron density $\rho_2$), was used as a model in the fitting process. The accumulation of electron-rich ester groups at crystal boundaries (and the possible local accumulation of branches) is expected to increase the density of the borders of the lamellae with respect to the cores.

The scattering was computed using the model of Zernike and Prins$^{6,7}$:

$$I(s) = Z(s) \cdot |f(s)|^2$$

with $Z(s)$ the interference function due to the repetition of lamellae, $f^2(s)$ the square of the norm of the shape factor of the lamellae, and $s = 2.\sin(\theta)/\lambda$, where $\theta$ is half the scattering angle and $\lambda$ the wavelength. The shape factor of the lamellae may be written as follows:

$$f(s) = 1/(\pi s) \left( \rho_1 \sin(\pi s z_1) + \rho_2 \left[ \sin(\pi s (z_1+2z_2)) - \sin(\pi s z_1) \right] \right)$$

In order to obtain $Z(s)$, the long period (i.e., the distance between two successive crystalline lamellae) was assumed to be distributed according to a sum of maximum two Gaussian functions. Truncation of the Gaussians for distances below $z_1+2z_2$ guaranteed that positive values be obtained for the thickness of the amorphous regions. The Fourier transform of the resulting distribution, $F(s)$, was computed numerically$^8$ and used to obtain the interference function:

$$Z(s) = \text{Re}\{(1 + F(s)) / (1 - F(s))\}.$$
The scattering was then convoluted by a Gaussian of standard deviation $\sigma$, which represents the effect of finite stack size, plus minor experimental effects not taken into account when desmearing experimental data. For a few incompletely crystallised samples, the scattering also displays a strong central scattering due to the contrast between lamellar stacks of finite size and the surrounding amorphous background. In such cases, this central scattering was modeled by a Gaussian function centered at the origin and of the same width as the convolution Gaussian. Parameters in the model are $z_1$, $z_2$, $\rho_1$, $\rho_2$, the width, height and location of the Gaussian(s) representing the distribution of long period, the width of the convolution Gaussian and the height of the central Gaussian if needed. An examination of the interference function $Z(s)$ and shape factor of the lamellae $f^2(s)$ reveals that the first peak in the scattering function is dominated by $Z(s)$ while the final peak is dominated by $f^2(s)$. Interestingly, the minima in the scattering function coincide with the minima of the lamellar shape factor, which periodically returns to near zero values, in opposite behavior to the interference function. This fact guarantees a high accuracy on the computed values of lamellar thickness.

A lamellar thickness can be defined in several ways, depending on which part of the more electron-rich region at crystal surface is considered to belong to the crystal. In this paper, lamellar thickness was defined as $z_1 + z_2$, i.e., the distance between the centers of the more electron-rich regions. Other definitions of $L_c$ were considered, essentially leading to conclusions similar to the ones drawn from the definition adopted in the paper.
**Figure S1.** Typical example of analysis of the SAXS of a P44/5-Prop sample.

**Top.** Proposed model of electron density of lamellae, used to compute the scattering. **Bottom.** Experimental Lorentz-corrected diffractogram for P44/5-Prop isothermally crystallised at 87°C for 10 minutes and fitted curve (displaced vertically for clarity purpose). **Middle.** Lamellar shape factor \( f^2(s) \) and interference function \( Z(s) \) as obtained from the fit.

**Correlation functions.** Normalised one-dimensional correlation functions were computed by Fourier transformation of the Lorentz-corrected SAXS data after apodization. The correlation function of the fits were also calculated and
compared to the experimental correlation function, in order to judge fit quality in both direct and reciprocal spaces.

**Fit results.** Table S1 lists the principal fit parameters ($\sigma$, $z_1$, $z_2$ and $\rho_2/\rho_1$) of the scattering curves of the sample of **Fig. 3e** of the paper (a sample cooled and reheated in a stepwise fashion in the X-ray beam). Because the scattered intensity was not measured in absolute units, only the ratio $\rho_2/\rho_1$ is relevant and given in Table S1.

**Table S1.** Selected fit parameters of the SAXS of the sample of **Fig. 3e** (sample cooled and reheated in a stepwise fashion in the X-ray beam). $T$ is the measurement temperature. Other parameters are defined in the text and **Fig. S1**.

<table>
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<tr>
<th>$T$ (°C)</th>
<th>$\sigma$ (nm$^{-1}$)</th>
<th>$z_1$ (nm)</th>
<th>$z_2$ (nm)</th>
<th>$\rho_2/\rho_1$</th>
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<td>0.0154</td>
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The fit parameters obtained for the samples of Fig. 3d (samples crystallised at different temperatures and measured at room temperature) are virtually identical to the ones of the sample of Table S1 measured at 41.7°C; they are not reported here for concision. The parameters serving to describe the distributions of long period (i.e., the distance between successive crystals) are not reported in the Table. Instead, the distributions of long period $P(L_p)$ obtained by the fitting routine are presented in Fig. S2.

**Figure S2.** Distributions of long period ($L_p$) of the $P44/5$-Prop sample of Fig. 3e (sample cooled and reheated in a stepwise fashion in the X-ray beam). The top and bottom graphs correspond to cooling and subsequent reheating steps, respectively.
The shapes of these distributions, not the parameters used to construct them, are the physically significant inputs to the fit routine. At high temperature, a long-distance tail develops in the distributions of distance, due to random melting of lamellae in stacks. Lamellae do not melt at a single temperature, since their surface energies depend on constraints progressively developing in amorphous neighbouring regions during crystallisation.
6. Details on the morphology of P44/5

A P44/5 sample (P44/5A) was crystallised by rapid cooling (-10°C/min) from the molten state (120°C) to room temperature. DSC heating thermograms of this sample are presented in Fig. S3 for different heating rates. The sample exhibits two melting endotherms (91-93°C and 100-102°C), separated by a prominent recrystallisation exotherm for the lowest heating rate. The high temperature exotherm vanishes for the highest heating rate, indicating that this peak results from melting/recrystallisation during heating.

Figure S3. Thermal behaviour of P44/5: DSC heating thermograms of sample P44/5A (crystallised from the melt at –10°C/min) and sample P44/5B (crystallised by slow cooling at –0.77 °C/min and annealed for 150 min. at 86.7°C). The heating rates are indicated in the figure. The lower and upper melting peaks correspond to crystals of type I and II, respectively.
Consequently, sample P44/5A may be considered to consist essentially of crystals of type I which melt upon heating at about 91°C. If given enough time, the melt recrystallises during heating into type II crystals which subsequently melt at about 100°C.

Another P44/5 sample (P44/5B) was crystallised by slow cooling (-0.77°C/min) from 120°C to 86.7°C, where it was held for 150 min. before being rapidly cooled to room temperature. The DSC thermogram of this sample is also presented in Fig. S3. Comparing the thermograms of samples P44/5A and B, it is obvious that sample B essentially consists of type II crystals (melting at about 100.5°C), and of a small amount of type I crystals (melting at about 93°C), probably formed during the final cooling of the sample to room temperature.

The Lorentz-corrected SAXS patterns of samples P44/5A and B are presented in Fig. S4 (left). The diffractograms exhibit a first peak of variable intensity and position, corresponding to the repetition of crystalline lamellae in stacks (with long periods of 10.4 and 15.6 nm found for samples A and B, respectively). This peak is followed by three peaks of decreasing intensity, arising from correlation between the location of ester planes in crystals (and, to a lesser extent, from crystal to crystal), corresponding to ester-ester repeat distances of 4.6 and 4.9 nm for samples A and B, respectively. The slight difference in the ester-ester repeat distances between the two samples results either from slight variations in the tilt angle of the chain axes versus the normal to the ester planes, or from limited distortions of chain conformation.
**Figure S4.** SAXS results for sample **P44/5A** (crystallised from the melt at –10°C/min) and sample **P44/5B** (crystallised by slow cooling at –0.77 °C/min and annealed for 150 min. at 86.7°C).

**Left.** Lorentz-corrected SAXS intensity.

**Right.** Corresponding one-dimensional correlation functions. The dotted lines correspond to correlation functions computed from the first SAXS reflection only, providing information on the correlation between successive crystals in stacks. The complete correlation functions are dominated by correlation between ester planes.

The one-dimensional correlation functions computed from the SAXS intensity are presented in **Fig. S4** (right). Strong correlation between ester planes are clearly seen in this figure, extending over 10 and 15 nm for sample A and B, respectively. The correlation functions computed from the first peak of the...
SAXS signal only ($\gamma_{11}(r)$) are also presented as dotted lines; these functions indicate the correlation between the location of successive crystals in stacks, not taking into account the presence of electron-rich ester planes. From $\gamma_{11}$, using standard procedures\textsuperscript{9}, a crystal thickness of about 4.9 nm is obtained for sample A which contains type I P44/5 crystals. This is very close to the thickness of P44/5-Prop crystals, suggesting that type I crystals have a thickness corresponding to one (tilted) monomer unit, similarly to P44/5-Prop. This is also supported by the close similarity of the correlation functions of samples P44/5-Prop and P44/5A (compare Fig. S4 with Fig. 3).

By contrast, the standard analysis of $\gamma_{11}$ of sample P44/5B, which essentially consists of type II P44/5 crystals, provides two possible values for the crystal thickness: 5.3 and 9.8 nm. This uncertainty follows from Babinet's principle\textsuperscript{10}. However, since the melting temperatures of type I and II crystals differ by about 10°C, and because the WAXS spectra of both samples do not indicate any evidence for polymorphism, type II crystals must by necessity be significantly thicker than type I crystals. This is supported by the complete correlation functions which indicate that correlation between positions of ester planes extends over longer distances for sample B than for sample A (by about 5 nm, close to the length of one tilted monomer unit). Therefore, one can safely conclude that the thickness of type II crystals is 9.8 nm, close to the length of two (tilted) monomer units.

Summing up, these experiments indicate the occurrence of at least two types of crystals for P44/5. These two types can be attributed to quantised variations of the thickness of crystals corresponding to the inclusion in the crystals of integral
numbers of monomer units. Similar results were obtained for P22/5 and have been published elsewhere\textsuperscript{1}. These experiments also show that control of the thickness of the crystal is not achieved with the linear polymer, as opposed to the branched one.
References


