# Supporting Information

## The influence of small amounts of linear polycaprolactone chains on the crystallization of cyclic analogue molecules

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**Avrami Fit**

The Avrami Fit was performed using an Origin® software application called *Polymer Crystallization Plugin*. This Origin® plugin was developed by Lorenzo *et al.* (Polymer Testing **26** (2007) 222). The Plugin is offered free upon request to Prof. A.J. Müller.

The data obtained by isothermal Differential Scanning Calorimetry (DSC) tests were used to perform the Avrami Fits. The parameters obtained are show from Table S1 to Table S2.

**Table S1.** Parameters Obtained by Fitting the Avrami Theory to the 3kg/mol samples (e.g., Data Shown in Figure 9a).

| Sample | $T_c$ (°C) | $n$ | $K$ x$10^5$ ($min^{-n}$) | $K^{1/n}$x$10^3$ ($min^{-1}$) | $\tau_{1/2t}$ (min) | $\tau_{1/2e}$ (min) | $1/\tau_{50\%}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|---|---|
| C–PCL 3k | 45 | 3.6 | 20064 | 640 | 1.41 | 1.45 | 0.69 | 1.0000 |
| | 46 | 3.2 | 10307 | 492 | 1.81 | 1.83 | 0.55 | 1.0000 |
| | 47 | 3.4 | 2818 | 350 | 2.56 | 2.60 | 0.39 | 1.0000 |
| | 48 | 3.7 | 501 | 239 | 3.72 | 3.83 | 0.26 | 1.0000 |
| | 49 | 3.3 | 448 | 194 | 4.72 | 4.82 | 0.21 | 1.0000 |
| | 50 | 3.3 | 129 | 133 | 6.74 | 6.95 | 0.14 | 1.0000 |
| | 51 | 3.1 | 72 | 97 | 9.05 | 9.20 | 0.11 | 1.0000 |
| | 52 | 3.2 | 18 | 68 | 13.08 | 13.35 | 0.08 | 1.0000 |
| | 53 | 2.9 | 15 | 48 | 18.41 | 18.52 | 0.05 | 0.9999 |
| C/L 95/5 3k | 40 | 3.1 | 112843 | 1040 | 0.86 | 0.87 | 1.15 | 1.0000 |
| | 41 | 3.0 | 43520 | 758 | 1.17 | 1.17 | 0.86 | 0.9999 |
| | 42 | 3.2 | 13280 | 532 | 1.69 | 1.70 | 0.59 | 1.0000 |
| | 43 | 3.0 | 5644 | 384 | 2.30 | 2.28 | 0.44 | 0.9999 |
| | 44 | 3.0 | 2043 | 273 | 3.24 | 3.22 | 0.31 | 0.9999 |
| | 45 | 3.0 | 649 | 187 | 4.73 | 4.73 | 0.21 | 0.9999 |
| | 46 | 3.1 | 181 | 130 | 6.87 | 6.93 | 0.14 | 1.0000 |
| | 47 | 2.7 | 184 | 97 | 9.28 | 9.25 | 0.11 | 0.9999 |
| C/L 90/10 3k | 39 | 3.1 | 216424 | 1283 | 0.70 | 0.72 | 1.39 | 1.0000 |
| | 40 | 3.5 | 74904 | 921 | 0.98 | 1.02 | 0.98 | 1.0000 |
| | 41 | 3.3 | 31175 | 702 | 1.27 | 1.28 | 0.78 | 1.0000 |
| | 42 | 3.3 | 12744 | 536 | 1.67 | 1.68 | 0.59 | 1.0000 |
| | 43 | 3.5 | 3428 | 381 | 2.34 | 2.37 | 0.42 | 1.0000 |
| | 44 | 3.7 | 984 | 287 | 3.20 | 3.27 | 0.31 | 1.0000 |
| | 45 | 3.5 | 437 | 212 | 4.23 | 4.33 | 0.23 | 1.0000 |
| | 46 | 3.8 | 63 | 144 | 6.20 | 6.40 | 0.16 | 1.0000 |
| | 42 | 3.0 | 116916 | 1053 | 0.84 | 0.87 | 1.15 | 1.0000 |
| | 43 | 3.4 | 35200 | 736 | 1.22 | 1.28 | 0.78 | 1.0000 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C/L 80/20 3k | 44 | 3.4 | 11989 | 536 | 1.68 | 1.77 | 0.57 | 1.0000 |
| | 45 | 3.5 | 3281 | 377 | 2.38 | 2.50 | 0.40 | 1.0000 |
| | 46 | 3.5 | 1200 | 283 | 3.24 | 3.42 | 0.29 | 1.0000 |
| | 47 | 3.8 | 157 | 183 | 4.93 | 5.25 | 0.19 | 1.0000 |
| | 48 | 3.9 | 29 | 124 | 7.13 | 7.62 | 0.13 | 0.9999 |
| | 49 | 3.6 | 18 | 91 | 9.81 | 10.47 | 0.10 | 1.0000 |
| | 50 | 3.8 | 3 | 65 | 13.92 | 14.58 | 0.07 | 1.0000 |
| L–PCL 3k | 37 | 2.5 | 51106 | 765 | 1.13 | 1.22 | 0.82 | 0.9989 |
| | 38 | 2.2 | 23699 | 520 | 1.61 | 1.70 | 0.59 | 0.9995 |
| | 39 | 2.4 | 9735 | 379 | 2.30 | 2.45 | 0.41 | 0.9995 |
| | 40 | 2.4 | 4022 | 262 | 3.33 | 3.57 | 0.28 | 0.9996 |
| | 41 | 2.4 | 1429 | 170 | 5.02 | 5.42 | 0.18 | 0.9997 |
| | 42 | 2.4 | 570 | 116 | 7.25 | 7.82 | 0.13 | 0.9996 |
| | 43 | 2.4 | 236 | 80 | 11.18 | 12.03 | 0.08 | 0.9998 |

**Table S2.** Parameters Obtained by Fitting the Avrami Theory to 12 kg/mol samples (e.g., the Data Shown in Figure 9b).

| Sample | $T_c$ (°C) | $n$ | $K$ x$10^5$ ($min^{-n}$) | $K^{1/n}$x$10^3$ ($min^{-1}$) | $\tau_{1/2\,t}$ (min) | $\tau_{1/2e}$ (min) | $1/\tau_{50\%}$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|---|---|
| C–PCL 12k | 39 | 2.8 | 31986 | 666 | 1.32 | 1.35 | 0.74 | 1.0000 |
| | 40 | 3.0 | 14227 | 522 | 1.69 | 1.73 | 0.58 | 1.0000 |
| | 41 | 3.2 | 5862 | 412 | 2.19 | 2.25 | 0.44 | 1.0000 |
| | 42 | 3.2 | 2652 | 322 | 2.81 | 2.87 | 0.35 | 1.0000 |
| | 43 | 3.3 | 807 | 232 | 3.79 | 3.88 | 0.26 | 1.0000 |
| | 44 | 3.2 | 384 | 176 | 4.98 | 5.07 | 0.20 | 1.0000 |
| | 45 | 3.3 | 131 | 134 | 6.84 | 6.97 | 0.14 | 1.0000 |
| | 46 | 3.3 | 43 | 95 | 9.69 | 9.87 | 0.10 | 1.0000 |
| | 47 | 3.3 | 11 | 63 | 14.13 | 14.32 | 0.07 | 1.0000 |
| | 48 | 3.7 | 0.7 | 40 | 21.92 | 22.60 | 0.04 | 1.0000 |
| | 49 | 3.5 | 0.3 | 26 | 32.86 | 33.32 | 0.03 | 1.0000 |
| C/L 95/5 12k | 36 | 2.3 | 56892 | 783 | 1.09 | 1.05 | 0.95 | 0.9998 |
| | 37 | 2.3 | 30308 | 595 | 1.44 | 1.37 | 0.73 | 0.9998 |
| | 38 | 2.3 | 15475 | 444 | 1.91 | 1.83 | 0.55 | 0.9999 |
| | 39 | 2.3 | 8868 | 349 | 2.45 | 2.35 | 0.43 | 0.9999 |
| | 40 | 2.5 | 3448 | 260 | 3.33 | 3.27 | 0.31 | 1.0000 |
| | 41 | 2.5 | 1563 | 189 | 4.48 | 4.42 | 0.23 | 1.0000 |
| | 42 | 2.5 | 898 | 152 | 5.85 | 5.78 | 0.17 | 1.0000 |
| | 43 | 2.4 | 548 | 114 | 7.82 | 7.67 | 0.13 | 1.0000 |
| | 44 | 2.6 | 139 | 80 | 11.29 | 11.28 | 0.09 | 1.0000 |
| | 45 | 2.7 | 37 | 54 | 16.52 | 16.58 | 0.06 | 0.9999 |
| C/L 90/10 12k | 38 | 2.6 | 22017 | 559 | 1.57 | 1.53 | 0.65 | 1.0000 |
| | 39 | 2.5 | 13825 | 453 | 1.92 | 1.88 | 0.53 | 0.9999 |
| | 40 | 2.7 | 5467 | 341 | 2.56 | 2.55 | 0.39 | 1.0000 |
| | 41 | 2.8 | 2216 | 257 | 3.36 | 3.37 | 0.30 | 1.0000 |
| | 42 | 3.0 | 754 | 196 | 4.54 | 4.57 | 0.22 | 1.0000 |
| | 43 | 3.2 | 201 | 144 | 6.27 | 6.35 | 0.16 | 1.0000 |
| | 44 | 3.2 | 67 | 102 | 8.67 | 8.77 | 0.11 | 1.0000 |
| | 45 | 3.3 | 15 | 69 | 12.48 | 12.65 | 0.08 | 1.0000 |
| | 46 | 2.4 | 12 | 23 | 13.68 | 13.48 | 0.07 | 0.9998 |
| C/L 80/20 12k | 38 | 2.6 | 81841 | 926 | 0.94 | 0.95 | 1.05 | 1.0000 |
| | 39 | 3.0 | 32872 | 690 | 1.28 | 1.32 | 0.76 | 1.0000 |
| | 40 | 3.1 | 13406 | 523 | 1.69 | 1.75 | 0.57 | 1.0000 |
| | 41 | 3.4 | 4342 | 397 | 2.27 | 2.33 | 0.43 | 1.0000 |
| | 42 | 3.4 | 1598 | 296 | 3.00 | 3.07 | 0.33 | 1.0000 |
| | 43 | 3.3 | 704 | 223 | 3.98 | 4.05 | 0.25 | 1.0000 |
| | 44 | 3.5 | 166 | 161 | 5.60 | 5.70 | 0.18 | 1.0000 |
| | 45 | 3.8 | 25 | 113 | 8.10 | 8.30 | 0.12 | 1.0000 |
| | 37 | 2.3 | 15450 | 444 | 1.90 | 1.87 | 0.54 | 0.9999 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| L–PCL 12k | 38 | 2.4 | 6806 | 326 | 2.61 | 2.58 | 0.39 | 0.9999 |
| | 39 | 2.4 | 3289 | 241 | 3.52 | 3.50 | 0.29 | 1.0000 |
| | 40 | 2.3 | 2052 | 185 | 4.54 | 4.50 | 0.22 | 1.0000 |
| | 41 | 2.5 | 735 | 140 | 6.19 | 6.20 | 0.16 | 1.0000 |
| | 42 | 2.4 | 411 | 101 | 8.25 | 8.30 | 0.12 | 1.0000 |
| | 43 | 2.4 | 221 | 78 | 11.03 | 11.13 | 0.09 | 1.0000 |
| | 44 | 2.3 | 128 | 55 | 15.38 | 15.43 | 0.07 | 1.0000 |

**Lauritzen and Hoffman Fit**

This Origin® plugin can be used not only to perform Avrami Fits but also to perform the Lauritzen–Hoffman Crystallization Fits. The parameters obtained from the LH theory are shown in Table S3.

**Table S3.** Parameters Obtained from Fitting the Lauritzen and Hoffman Theory to the Data of Figure 7.

| Sample | $K_g^{\tau}$ ($K^2$) | $\sigma_e$ (erg/cm$^2$) | $R^2$ |
|---|---|---|---|
| C–PCL 3k | 236319 | 254 | 0.99681 |
| C/L 3k 95/5 | 329576 | 346 | 0.99711 |
| C/L 3k 90/10 | 307817 | 315 | 0.99882 |
| C/L 3k 80/20 | 297044 | 287 | 0.98808 |
| L–PCL 3k | 247079 | 274 | 0.99904 |
| C–PCL 12k | 298825 | 321 | 0.99904 |
| C/L 12k 95/5 | 334344 | 351 | 0.99935 |
| C/L 12k 90/10 | 307017 | 314 | 0.99434 |
| C/L 12k 80/20 | 317940 | 310 | 0.99829 |
| L–PCL 12k | 186314 | 207 | 0.99439 |

**Successive Self-Nucleation and Annealing (SSA)**

The SSA experiments were performed with a fractionation windows of 3 ºC in 3 kg/mol sample.

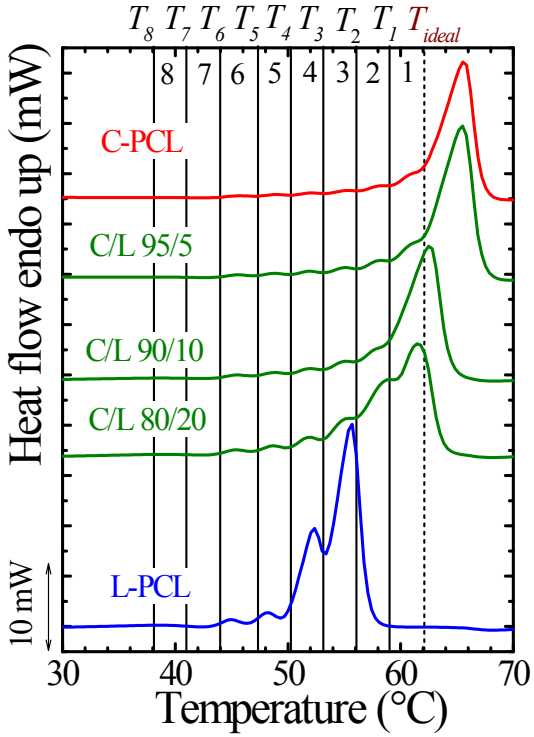


**Figure S1.** Final heating scan run after SSA thermal fractionation for C and L-PCLs and their C/L blends of 3kg/mol. The fractionation window was 3 ºC. Red and blue curves represent C-PCL and L-PCL, respectively, whereas green curves represent the C/L blends.