

Crystallization kinetics of polytridecanolactone and polypentadecanolactone

Peter Skoglund and Åke Fransson*

Department of Applied Physics and Electronics, Umeå University, SE-901 87 Umeå, Sweden

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The crystallization kinetics of fractionated samples of polytridecanolactone and polypentadecanolactone have been investigated and compared. The general constitutional repeating unit is $[(\text{CH}_2)_n\text{CO}-\text{O}]$, where n is 12 and 14 for PTDL and PPDL respectively. Equilibrium melting points have been deduced by the Hoffman–Week extrapolation method and found to be close to 364 K and 370 K, respectively. The Lauritzen–Hoffman theory of crystal growth is applied to the data and the extracted nucleation parameters are compared with the ones for polyethylene. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polycaprolactone (PCL) is a biodegradable synthetic polymer for which a number of technical implementations have been proposed^{1–5}. The general monomer structure for this type of linear aliphatic polyester is $-\text{[(CH}_2)_n\text{CO}-\text{O}]_n-$, where n is the number of ethylene units between each (CO–O) group and equals 5 for PCL. In a previous paper⁶, we have analyzed the crystallization process of five molecular weight PCL samples. Other interesting polymers in the lactone group are polytridecanolactone (PTDL) and polypentadecanolactone (PPDL), where the subscript n is 12 and 14, respectively. The properties of these higher polylactones are, however, largely unknown. In an earlier publication⁷, we discussed the properties of a broad molecular weight distribution sample of PPDL. In this paper, we present thermodynamic data and crystallization kinetics of fractionated samples of polytridecanolactone and polypentadecanolactone.

EXPERIMENTAL

The measurements were done with a Perkin-Elmer Differential Scanning Calorimeter (DSC-2), equipped with the intracooler II cooling system and with nitrogen as a purge gas. Calibrations were done according to methods described by Höhne *et al.*⁸ Unless otherwise is mentioned, melting points are defined as the intersection between the extrapolated melting peak and the sample base line. The reported enthalpy changes are calculated according to the total enthalpy method as described by Gedde⁹.

Two samples of polytridecanolactone labelled PTDL-A and PTDL-B and two samples of polypentadecanolactone, PPDL-A and PPDL-B were encapsulated in standard aluminium pans. The sample masses were between 2 and 5 mg and no mass changes were detected after the experiments. The molecular characteristics of the discussed samples, as determined by size exclusion chromatography by Polymer Source Inc., Dorval, Canada, are shown in Table 1.

Table 1 Molecular weight characteristics for the samples, as determined by size exclusion chromatography

Sample code	M_n	M_w	M_z	M_w/M_n
PTDL-A	11 000	13 600	16 200	1.24
PTDL-B	17 800	20 900	24 000	1.17
PPDL-A	10 700	14 500	18 700	1.36
PPDL-B	18 700	36 300	60 200	1.94

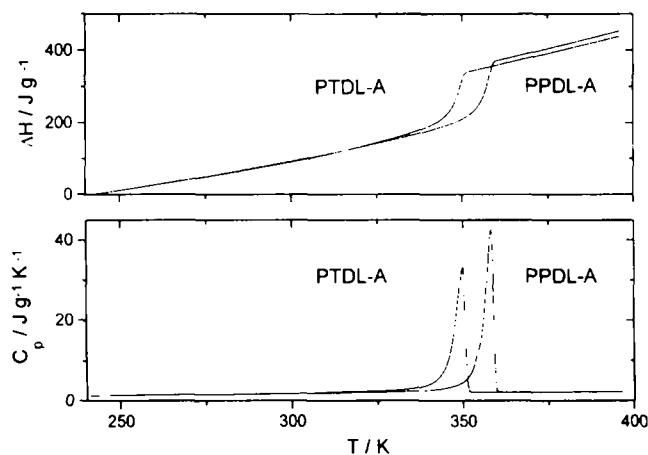


Figure 1 Specific heat capacity and corresponding integrated enthalpy for samples PTDL-A and PPDL-A of similar molecular distribution

RESULTS AND DISCUSSION

Due to the long run of ethylene units separating the CO–O groups, it is expected that both polymers should exhibit polyethylene like properties. It is, for example, known^{10,11} that PCL with five CH₂ groups, already has a fold surface energy close to that of polyethylene. The heat of melting and the melting temperature are both expected to be slightly higher for PPDL than for PTDL, but less than the values found for polyethylene.

In Figure 1, we show specific heat capacity and corresponding integrated enthalpy curves for PTDL-A and PPDL-A samples of similar molecular weight distributions.

* To whom correspondence should be addressed

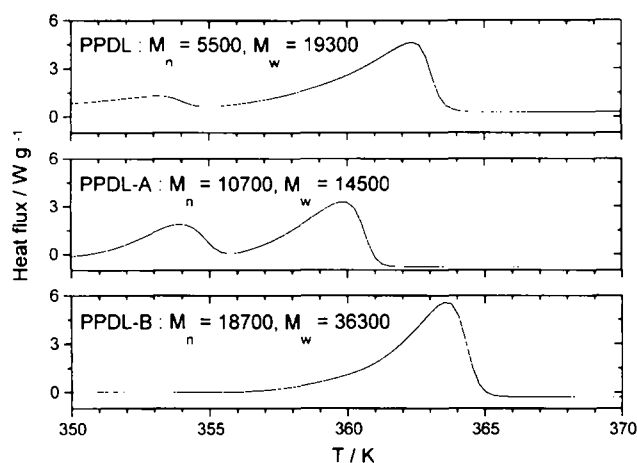


Figure 2 The melting peaks found after isothermal crystallization at 352 K for 16 min followed by rapid cooling to 300 K; the data were recorded at a heating rate of 10 K/min

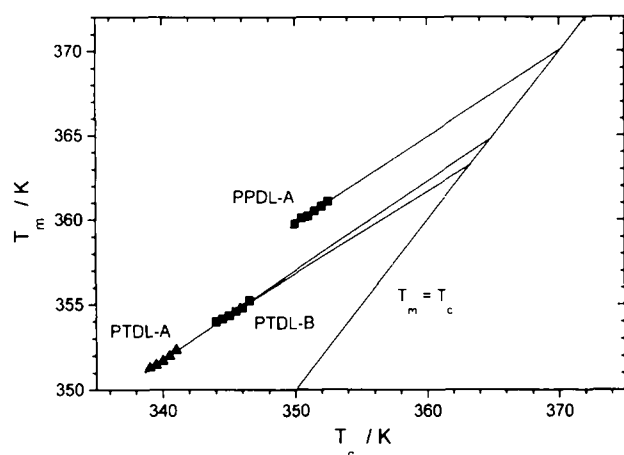


Figure 3 End melting points as a function of crystallization temperature; all measurements were done at a heating rate of 5 K/min; the Hoffman–Week equilibrium point is found at the crosspoint of the extrapolated lines with the $T_m = T_c$ line

The data are measured at a heating rate of 10 K/min, and found after 5 min annealing in the melt at 400 K followed by cooling with 80 K/min to 230 K. As seen after this treatment, the PTDL-A sample has a slightly lower melting point and melting enthalpy than PPDL-A. The heat of melting for PTDL-A is 141 J/g, while the onset melting temperature is 345.3 K and the peak value 349.3 K. The corresponding data for the PPDL-A sample are 151 J/g with an onset melting of 354.5 K and a peak temperature of 358.0 K.

For a totally crystalline material Wunderlich¹² gives a heat of melting of 238 J/g for PTDL and 264 J/g for PPDL, while Lebedev and Yevstropov¹³ give values of 216 J/g and 233 J/g, respectively. By using an adiabatic calorimeter and a method based on fractional melting they find equilibrium melting temperatures of 368 ± 1 K for PTDL and 370.5 ± 1 K for PPDL. Unfortunately, no molecular weight distributions were given for their samples, but their viscosity data indicate higher molecular weights than our samples. For comparison, the corresponding values for polyethylene¹² are 293 J/g and 415 K.

From the above values of the heat of melting for a totally crystalline material, we find a crystallinity degree close to 65% for both of our samples. Due to the high degrees of

crystallinity, only very weak glass transitions are spotted at about 250 K for PPDL-A and 240 K for PTDL-A. This indicates that a substantial part of the non crystalline portions are rigid, i.e. trapped by the crystalline phase.

In a previous paper⁷ on a broader molecular weight sample of PPDL, with $M_n = 5500$, $M_w = 19\,300$ and $M_z = 48\,300$, we found segregation into crystals of different melting points. For example, after isothermal crystallization at 352 K for 16 min followed by cooling to 300 K and a subsequent melting scan double melting peaks appeared. This segregation effect is also seen in the PPDL-A sample after the same treatment. For the PPDL-B sample, of both higher and broader molecular weight distribution, only a single melting peak was observed. In Figure 2, we show the melting scans of the three different samples where the DSC signals here have been normalized with respect to sample mass. It is clear that the segregation decreases for samples of high molecular weight.

In order to proceed with the analysis, we have used the Hoffman–Week extrapolation method^{9,14} for extraction of the equilibrium melting points. According to this approach, the relation between the melting temperature, T_m found after isothermal crystallization at T_c can be written as in equation (1). Here T_m^0 is the equilibrium melting point and β is the ratio of the crystal thickness to the initial thickness of the nucleus,

$$T_m = T_m^0 \left(1 - \frac{1}{\beta}\right) + \frac{T_c}{\beta} \quad (1)$$

From a plot of the melting points as a function of the crystallization temperature we evaluate the slope $1/\beta$. Since equilibrium crystals melt at the crystallization temperature, the equilibrium melting temperature can be found by extrapolating the slope to the point of intersection with the line $T_m = T_c$. It is known that the recorded melting points depend on the heating rate and time of crystallization at T_c . We have chosen to record the end points of the melting peaks, which usually show a high reproducibility, here taken at a heating rate of 5 K/min.

It is further assumed that the thickening rate of the crystals at T_c is proportional to the crystallization rate itself, and the isothermal crystallization time is therefore set to be 3 times the half crystallization time. In Figure 3, we show the linear parts, with a constant β , of a plot of T_m versus T_c for PTDL-A, PTDL-B and PPDL-A.

As seen, the extrapolated equilibrium melting temperature for the PPDL-A sample is close to 370 K. The PPDL sample reported in the previous paper⁷ shows a similar equilibrium melting point of 370 K. It must, however, be emphasised that the rather long extrapolation gives an uncertainty in the equilibrium melting temperature. For example, a 95% confidence band gives for the PPDL-A sample a variation of T_m^0 from 367 K to 374 K. However, in a single other paper found, presenting experimental data concerning PPDL and PTDL, Lebedev and Yevstropov¹³ give, as mentioned above, an equilibrium melting point of 370.5 K. Their value was found by using an adiabatic calorimeter and is very close to the value given here. The PTDL-A and PTDL-B samples show lower extrapolated equilibrium melting points with an average of about 364 K. It is noted that PTDL-A, of lower molecular weight, needs a larger supercooling to crystallize than PTDL-B. The corresponding value for PTDL measured by Lebedev and Yevstropov¹³ was 368 ± 1 K.

By using the Lauritzen–Hoffman (LH) model¹⁴ for

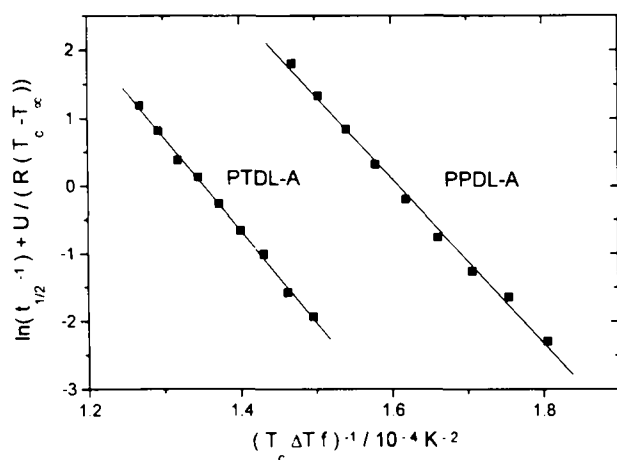


Figure 4 Kinetic analyses of the crystallization according to equation (2) for the samples PTDL-A and PPDL-A: the slope is equal to the nucleation parameter k_g

crystal growth, the following equation can be shown to be valid if the number of primary nucleation centres are mainly independent of temperature and become active simultaneously,

$$\frac{1}{t_{1/2}} = C \left[\exp\left(\frac{-U}{R(T_c - T_x)}\right) \exp\left(\frac{-k_g}{T_c \Delta T f}\right) \right] \quad (2)$$

Here $t_{1/2}$ is the time at which 50% of the final crystallinity is obtained and C is a constant. The first exponential gives the short range mass transport across the melt/crystal interface and the second exponential shows the surface nucleation behaviour. In the first exponential, U is the activation energy for mass transport across the crystallizing interface, R the gas constant, T_x a temperature where all segmental motion has ceased, and T_c , finally, is the crystallization temperature.

According to Hoffman *et al.*¹⁴, the value of U for a typical linear polymer can be set to 6280 J/mol and T_x can be approximated with a temperature 30 K below the glass transition temperature, T_g . In the nucleation term, ΔT is the supercooling and f a correction factor for the temperature dependency of the heat of fusion, usually approximated with $2T_c/(T_c + T_m^0)$. The coefficient k_g is the nucleation constant and affects the growth rate of the crystals. It contains the ratio of surface energy and crystallization energy of the nucleus according to equation (3).

$$k_g = \frac{nb\gamma\gamma_c T_m^0}{k\Delta h_m^0} \quad (3)$$

Here n describes the growth regime, b the monolayer thickness and γ and γ_c the lateral and fold surface energies, respectively. Finally, k is the Boltzmann constant and Δh_m^0 is the heat of melting per unit volume. Three different growth regimes are defined by Hoffman *et al.*¹⁴, which differ according to the rate at which new nucleus are deposited on the crystal. In regime I, at high crystallization temperatures, the nucleation rate is low and only one nucleus causes the completion of the entire layer and here n equals 4. In regime II, at higher supercooling, multiple surface nucleus occur and become sites themselves for new nucleation and here n is 2. At even lower crystallization temperatures, the nucleation rate is very high and the distance between the surface nucleus becomes comparable to the width of the nucleus. In this regime the growth is again proportional to nucleation and n is 4.

Following equation (2), a plot of $\ln(1/t_{1/2}) + U/(R(T_c - T_x))$ versus $(T_c \Delta T f)^{-1}$, should, if the LH theory of crystallization is valid, give a straight line within a given growth regime. Accordingly, the slope of the line corresponds to the nucleation constant, k_g . In Figure 4 we show such plots for PTDL-A and PPDL-A. It is noted that the absolute value of the slope is very sensitive to the equilibrium melting temperature, and substantial differences may occur due to the uncertainty of the equilibrium melting point. However, no change of the slopes are seen indicating a constant nucleation regime. By using 370 K and 364 K, respectively, as the equilibrium melting points we find a k_g value close to $13 \times 10^4 K^2$ for PTDL-A and about $12 \times 10^4 K^2$ for PPDL-A. For the PPDL sample of broad molecular weight distribution, discussed earlier by us⁷, we found a nucleation parameter of $8.7 \times 10^4 K^2$. From the value of the nucleation parameter, the product of the surface energies can be evaluated from equation (3) if the nucleation regime is known.

It is well established^{9,14} that polyethylene with molecular weights between about 15 000 and 100 000 has a nucleation parameter of about $10 \times 10^4 K^2$ in regime II and close to $20 \times 10^4 K^2$ in regime I. For lower molecular weights the fold surface energy decreases, due to chain end effects, and thus the nucleation parameter. In comparison with polyethylene, it is expected that the inclusion of the COO groups in PTDL and PPDL would slightly decrease the surface energies. Lopez *et al.*¹⁵ investigated the crystallization of blends of fractions of linear polyethylene. They found that a mixture of 50% of a low molecular weight material with $M_w = 2500$ and 50% of a higher molecular weight of 66 000 only gave a minor lowering of the fold surface energy for the crystallizing (high molecular weight) component. This was interpreted as a consequence of the limited cocrystallization between the high and low molecular weight materials. Such limited cocrystallization could explain the lower nucleation parameter of $8.7 \times 10^4 K^2$ previously found for the lower and broader molecular distribution and the one found here for PPDL-A of $12 \times 10^4 K^2$. The similarity in chain configuration of PPDL, PTDL, and polyethylene, together with the nucleation constants found support that regime II growth dominates for PPDL and PTDL-A in the investigated temperature ranges. Again noting the sensitivity of the absolute value of the nucleation parameter to the choice of equilibrium melting point, we find that the k_g values mainly coincide with the ones given for regime II growth of polyethylene^{9,14,16}. The supercooling varies between 20–24 K and 16–20 K for PTDL-A and PPDL-A, respectively. For polyethylene fractions the transition between regime I and II growth is found at a supercooling of about 17.5 K^{9,14,16}.

The PTDL-B sample, with the most narrow molecular weight distribution, having a polydispersity index of 1.17 and a molecular weight average of 20 900, shows contrary to the other samples a change of the slope, as seen in Figure 5. Although the temperature range is rather small, between 345 K and 348 K, the k_g values of the high and low temperature slopes are $24.3 \times 10^4 K^2$ and $11.3 \times 10^4 K^2$, respectively giving a ratio of 2.1 which is very close to 2.0 as predicted by the LH theory. The lines break in the vicinity of 347 K or at a supercooling of 17 K by using 364 K as the equilibrium melting point. As mentioned above, the transition between regime I and II is for polyethylene found at a similar supercooling of 17.5 K.

The lack of regime transition for PTDL-A and PPDL-A could possibly be due to the somewhat higher supercooling

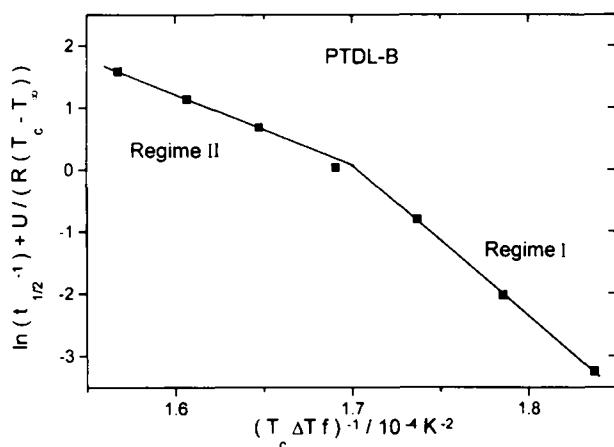


Figure 5 Kinetic analysis of the crystallization according to equation (2) for the sample PTDL-B; the intersection point of the two fitted lines indicate a transition from regime I to regime II growth

for these two samples. This would, in analogy with polyethylene, mainly give regime II crystallization. However, mixed crystallization regimes are discussed by Hoffman *et al.*^{14,16}, and also reported by Leung *et al.*¹⁷ for some solution crystallized fractions of polyethylene. Further, the lower molecular weight of PTDL-A and PPDL-A may, despite the rather narrow fraction, give molecules with different abilities to crystallize. Different crystallization rates will certainly smear out any transition as shown by Hoffman *et al.*¹⁶. The heat flux curve of PPDL-A in Figure 2 reveals a pronounced segregation effect. In such a case, the crystallization of the low molecular weight material is promoted by the presence of the earlier crystallized high molecular weight molecules.

SUMMARY

Two linear aliphatic polyesters with a general repeating unit $[(\text{CH}_2)_n\text{CO}-\text{O}]$, where n is 12 for polytridecanolactone and 14 for polypentadecanolactone have been investigated and compared with respect to thermodynamics and crystallization kinetics. It is found that both polymers are rapidly crystallizing with polyethylene-like properties. The equilibrium melting points have been determined with the Hoffman-Week extrapolation method and were found to

be 370 K for the PPDL-A sample and about 364 K for PTDL-A and PTDL-B. Using the crystal growth theory of Lauritzen and Hoffman we have found nucleation parameters for PTDL-A and PPDL-A, which basically are in agreement with that for regime II growth of polyethylene. The PTDL-B sample, having the most narrow molecular fraction ($M_n = 20\,900$ and polydispersity 1.17) shows a transition from regime I to regime II at a supercooling of about 17 K, which is very close to that found for polyethylene of 17.5 ± 1 K. None of the other two investigated samples (PTDL-A and PPDL-A) with an M_w of about 14 000 and polydispersity of 1.24 and 1.36, respectively, showed any change in nucleation parameter in the accessible temperature range.

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