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A Comparative Study on the Crystallization Behavior of Analogous Linear and Cyclic Poly(ε-caprolactones)

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S Supporting Information

In recent years there have been numerous studies on cyclic polymers.[1−8] These works have been focused on changes in glass transition temperatures,[1,5] melting temperatures,[7,8] crystal morphology,[1,6,9,10] and melt viscosity,[1,5,7,11,12] among other properties. Data are scarce regarding the comparison between linear and cyclic model polymers crystallization properties. The few comparisons available primarily focus on the lamellar morphology[9,10] and on the differences in melt viscosity.[1,7]

Several materials have been studied including poly(dimethylsiloxane), poly(ethylene oxide), polyethylene, and various aliphatic polyesters.[1,6,7,13−15] Most studies have employed low molecular weight materials,[1] largely because of synthetic difficulties in preparing well-defined, narrow polydispersity cyclic polymers without linear impurities.[16] Recently, Bielawski et al.[7] reported a major breakthrough using a cyclic Ru metathesis catalyst to prepare to generate high molecular weight cyclic polyethylene (PE) (M_n = 200 kg/mol) using a new ring expansion polymerization approach. Though the polydispersities were generally broad (>1.8), they reported a slight increase in melting temperature of the cyclic polymers (132 °C) with respect to that of a linear PE (130 °C). It is well-known that cyclic polymers have a lower viscosity in the melt as compared to linear polymers of similar chain lengths.[1,5,7] This effect is attributed to a smaller density of molecular entanglements due to the lack of chain ends.[1,5,7] Such variation in the number of entanglements per chain is expected to lead to differences in crystallization kinetics between cyclic and linear chains. Tezuka et al.[8] employed cyclic and linear poly(tetrahydrofuran), PTHF, and found a difference in the spherulitic growth rates as determined by polarized light optical microscopy (PLOM). Surprisingly, the cyclic polymer crystallized at a slower rate as compared to the linear one. This result is unexpected since the cyclic polymer should have a lower melt viscosity than the linear one. The authors proposed several explanations for this behavior: differences in conformational entropy of the chains in the molten state, an adsorption mechanism of the crystal growth front during the secondary nucleation process, or differences in chain folding surface energy.[8] In addition, Tezuka et al. reported that the melting temperature of cyclic PTHF was lower than its linear counterpart.

Recently, the cyclization of linear polymer precursors using the Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) reaction has become an attractive method for preparing cyclic polymers because already optimized linear polymerization chemistries can be used in concert with this efficient coupling reaction to generate high-purity cyclic polymers.[17] This approach enables the incorporation of diverse backbone chemistries into polymer macrocycles including atom transfer radical polymerization,[17−20] reversible addition−fragmentation chain transfer polymerization,[21,22] and ring-opening polymerizations.[23−25] This CuAAC cyclization route provides synthetic access to exact linear and cyclic analogues. Extensive characterization by GPC and MALDI-TOF MS confirmed the nearly quantitative cyclization of the linear precursors and verified the absence of any substantial amount of linear impurities.[23]

In the present work, we communicate the large differences that can be found in the overall crystallization kinetics (as determined by differential scanning calorimetry, DSC) and in the spherulitic growth rates (determined by PLOM) of linear and cyclic PCLs. Standard DSC runs also yielded differences in melting points for the two types of polymers revealing the large impact of molecular architecture on the thermal stability of the PCL crystals.

The materials employed were three cyclic PCLs with average number molecular weights (M_n) of 2, 4.9, and 7.5 kg/mol and two linear analogues of 2 and 7.5 kg/mol (their polydispersity indexes were lower than 1.2 for all samples). The linear analogues bore azide and hydroxyl end groups, except an additional sample of 2 kg/mol in which the alcohol end group was modified to the acetate; see Figure 2b (Table 1). Thermal characterization was performed with a PerkinElmer DSC PYRIS Diamond using ultrapure nitrogen as inert atmosphere. Isothermal crystallization as well as standard cooling and heating scans were evaluated for all PCL samples (nonisothermal measurements were performed at 20 °C/min). The morphology of each sample was also studied by PLOM, using a Zeiss MC-80 optical microscope with a Linkam TP-91 hot stage.

Figure 1a shows cooling scans from the melt after the thermal history was erased by keeping the sample at 90 °C for 3 min. The peak crystallization temperature (T_c) of the samples for the cyclic oligomers are much higher (5−10 °C) than their linear counterparts. The apparent peak melting temperatures (T_m) of the cyclic polymers (see Figure 1b) are also higher than the linear PCLs. While the melting peaks for the linear PCL exhibit substantial variation between the PCL-OH 2K and PCL-OH 7K

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Table 1. Number-Average Molecular Weight (M_n) and Polydispersity Index (PDI = M_w/M_n) Data for PCL Samples of Three Different Molecular Weights Studied

	M_n			PDI	
polymer	GPC[a]	GPC[b]	MALDI	GPC	MALDI
PCL-Acet 2K[c]	4580	2190	2360	1.11	1.02
PCL-OH 2K	4230	2010	2040	1.17	1.05
C-PCL 2K	3310	1550	2320	1.13	1.03
C-PCL 4.9K	6860	3390	5040	1.08	1.02
PCL-OH 7.5K	14700	7670	7340	1.13	1.02
C-PCL 7.5K	9500	4800	7000	1.11	1.04

[a] The data were calculated by gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization (MALDI) mass spectrometry. [b] Calibrated based upon linear poly(styrene) standards. [c] Corrected value for linear PCL,[26] using $M_n(\text{PCL}) = 0.259 M_n(\text{PS})^{1.073}$.

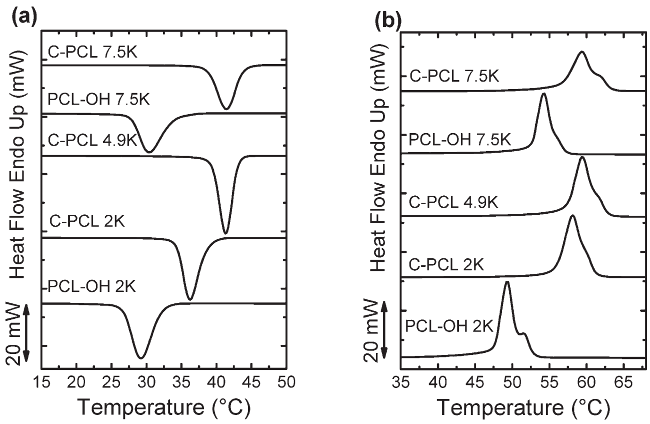

Figure 1. (a) DSC cooling scans after erasure of thermal history and (b) subsequent heating scans at a controlled rate of 20 °C/min.

(49−55 °C), the melting peaks of the cyclic PCLs exhibits less variation over the same molecular weight range (58.1−59.4 °C). Similar results have been reported previously for linear and cyclic poly(ethylene oxide)s by Cooke et al.[6]

The melting endotherms in Figure 1b exhibit a bimodal distribution of melting points due to partial melting and reorganization during the heating scan. This was demonstrated by performing experiments (not shown) at different cooling rates. As the cooling rate decreases, the sample can crystallize to a larger extent at higher temperatures, leading to more stable crystals that do not need to reorganize during the subsequent heating scan, therefore exhibiting unimodal melting traces. The degrees of crystallinity calculated from the DSC scans in Figure 1 yielded values in the range 50−70% for all samples.

The results of standard DSC scans indicate that the cyclic PCL chains can crystallize and melt at higher temperatures than linear analogues. The higher T_m values may be due to the formation of thicker crystals and/or to a lower entropy change of the cyclic chains upon melting as compared to the linear ones. Nevertheless, as pointed out below, we did not detect changes in the equilibrium melting points in between the linear and the cyclic PCLs, so the entropic differences may not be the dominating factor.

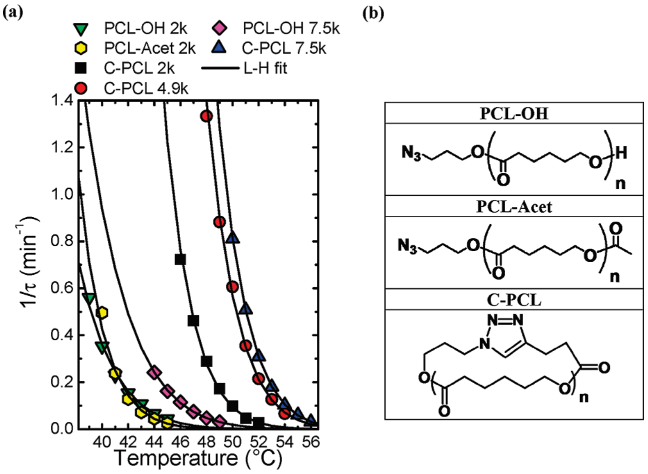

Figure 2. (a) Overall crystallization rate expressed as the inverse of half-crystallization time determined by isothermal DSC experiments for the indicated cyclic and linear PCL samples as a function of the crystallization temperature. (b) Chemical structures of the polymer samples used.

Figure 2a shows a summary of the results obtained by isothermal crystallization performed according to a previously reported protocol.[27] The inverse of the half-crystallization time is taken as an experimental measure of the overall crystallization rate (it includes contributions from both primary nucleation and crystal growth). The differences in crystallization kinetics between cyclic and linear PCLs samples are striking. It is clear that cyclic chains require lower undercoolings (or higher T_c values) in order to crystallize than linear PCL chains. Furthermore, the crystallization rate is much faster for cyclic PCL chains than for linear chains of identical length. For example, if the samples with M_n = 2 kg/mol are considered at a constant T_c value of 46 °C, cyclic PCL crystallizes at a rate faster by 1 order of magnitude in comparison to the rate exhibited by its linear counterpart. This large difference in crystallization rate was observed for all the samples examined in a rather small interval of molecular weights (i.e., 2−7.5 kg/mol).

In this low M_n range, the crystallization rate of PCL linear homopolymers increases with the molecular weight, since the overall crystallization kinetics is controlled by primary and secondary nucleation phenomena. At larger M_n values (typically above 20 kg/mol for PCL), the crystallization rate of linear PCL homopolymers becomes slower as the molecular weight increases, since the kinetics become dominated by diffusion (because the entanglement density as well as the melt viscosity increases with molecular weight). In other words, in the molecular weight range of the polymers employed here, molecular diffusion should be very easy; nevertheless, cyclic and linear polymers have different diffusion rates as will be discussed below.

We also calculated the value of the equilibrium melting point ($T_m°$) by employing the Hoffman−Weeks extrapolation procedure. The apparent T_m values used were those determined in a subsequent heating scan at 20 °C/min after the isothermal crystallization was saturated. We were not able to find significant differences in between the cyclic and the linear samples regarding the value of $T_m°$ considering the margin of error during extrapolation. For instance, the values of $T_m°$ were 81 °C for the cyclic sample with 7.5 kg/mol and 80 °C for the linear analogue. These values are within the range of values reported in the literature for

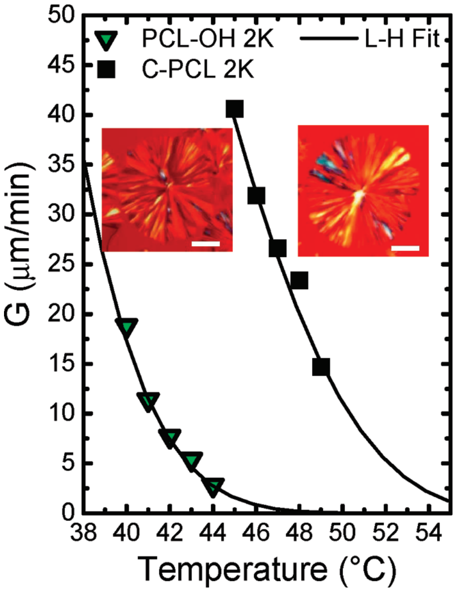

Figure 3. Spherulitic growth rate determined by PLOM for the indicated cyclic and linear PCL samples. The typical spherulitic morphologies obtained are also shown.

PCL samples (70−98 °C, see refs 28−30). Therefore, we do not consider intrinsic differences in T_m° as the cause for the different undercoolings at which the cyclic and the linear polymers crystallize.

The overall crystallization data can be well described by the Avrami equation in the primary crystallization range:[27]

$$1 - V_c(t) = \exp(-k(t - t_0)^n) \qquad (1)$$

where V_c is the relative volumetric transformed fraction (i.e., relative amount of material that has crystallized), t_0 is the induction time, n is the Avrami index, and k is the overall crystallization rate constant (i.e., it contains contributions from both nucleation and growth). We have employed a conversion range of 3−20% (i.e., relative volumetric fraction transformed to the crystalline state) for all samples where the fit of the Avrami equation is excellent.[27]

A table included in the Supporting Information (Table S) presents the values of the Avrami parameters k and n as well as the experimental values of the half-crystallization time, $\tau_{50\%}$, and theoretical values of this quantity estimated employing the fitted Avrami parameters.[27,31−33] A comparison between the experimental and the fitted $\tau_{50\%}$ values clearly indicate that they are quite similar, so that the Avrami equation holds reasonably well even up to 50% conversion (i.e., within the entire primary crystallization range). The Avrami index values can be generally approximated to the range 3−4. This means that instantaneously ($n = 3$) or sporadic ($n = 4$) spherulitic superstructures should be forming.[34] The presence of spherulites was indeed confirmed by PLOM observation (see examples in Figure 3).

Figure 3 shows spherulitic growth rate data for the cyclic 2 kg/mol PCL and its linear analogue. Both cyclic and linear PCLs exhibited well-developed negative spherulites without any banding. The trend observed in Figure 3 corresponds to the classic decrease in growth rate with T_c that is caused primarily by secondary nucleation control.[35] The growth rate is much faster (about 1 order of magnitude or more depending on T_c) for the cyclic polymer than for the linear analogue. This is consistent with Figure 2a and demonstrates that the growth rate is greatly affected by the cyclic chain configuration and therefore is an important parameter along with the nucleation rate. The effect of the nucleation rate was assessed in combination with the growth rate in Figure 2a when the overall crystallization kinetics (that includes nucleation and growth) was considered. The solid lines in Figures 2a and 3 correspond to fittings of the Lauritzen and Hoffman theory[34,35] for nucleation and growth which will not be treated here for the sake of brevity.

The critical molecular weight for the development of molecular entanglements in PCL has been estimated to be close to 2.3−3 kg/mol.[36,37] However, Izuka et al.[38] performed detailed rheological studies on PCL fractions and determined the following scaling laws for the melt zero-shear rate viscosity (η) with the weight-average molecular weight (from 2 to 20 kg/mol).

$$\eta \propto M_w^{2.15} \quad (\text{for } M_w \text{ values in the range } 2-7 \text{ kg/mol}) \qquad (2)$$

$$\eta \propto M_w^{3.4} \quad (\text{for } M_w > 7 \text{ kg/mol}) \qquad (3)$$

At M_w values larger than 7 kg/mol the scaling of the viscosity with M_w went up to 3.4 as expected for a highly entangled system. At values lower than 7 kg/mol the scaling exponent was not 1 as expected for entanglement-free melts, but an intermediate value of 2.15, which is not common. This confirms that the rheology of linear PCL belongs to a rare class of polymers which exhibit an intermediate M_w range (from 2 to 7 kg/mol) where the material is in the melt but apparently not completely free of entanglements.

Many reports have determined that entangled cyclic molecules in the molten state have much lower zero-shear viscosities than linear chains of the same molecular length.[11,38−42] Even in the case of unentangled cyclic polymers, the iso-free volume zero-shear viscosity has been reported to be half that of the linear polymer.[42] Therefore, molecular diffusion is expected to be much easier for rings than for linear polymers.[43] This fact has been proven experimentally on polystyrene rings where diffusion coefficients were higher by a factor of 2 as compared to linear chains[44] and also predicted theoretically.[12]

The results presented here can be explained by the improved chain diffusion resulting from the lack of chain ends and the cyclic topology in c-PCL. There have been theoretical predictions that indicate that cyclic polymeric chains tend to have more compact or collapsed random coil conformations than linear chains,[45−48] among other suggestions.[12] Nevertheless, their remarkable diffusion ability is probably the key factor behind their improved crystallization rate.

Annealing experiments (not shown here) demonstrated that the cyclic PCL samples employed in this work were capable of increasing their melting points even further. Such experiments indicate that even though the cyclic chains crystallized in thicker lamellae than their linear analogues during isothermal crystallization, they were able to undergo chain folding upon crystallization from the melt.

To confirm that the samples did not degrade during the crystallization experiments, and therefore that the unique measurements for the c-PCLs described above are truly the results of the cyclic topology, the samples were reanalyzed by MALDI-TOF MS and GPC after completion of the crystallization study. The MALDI-TOF MS exhibited the same molecular weights and residual masses observed for the starting materials,[49] and GPC traces also exhibited no sign of degradation.

The linear PCL samples employed in this study included a hydroxyl (−OH) group on the terminal chain end, which may hinder diffusion due to intermolecular hydrogen bonding.[50] However, we have performed crystallization kinetics experiments on identical molecular weight linear PCL chains but terminated with acetate groups ($O-CO-CH_3$) which cannot act as H-bond donors, yet the thermal characterization is nearly identical to the hydroxyl-terminated analogue. One example is presented in Figure 2a. Therefore, we believe that it is the chain topology that is causing the differences in crystallization kinetics and not the presence of a hydroxyl end group.

The results presented here demonstrate that cyclic PCL chains within the 2−7 kg/mol range can crystallize much faster than linear chains of identical molecular weight and can also form crystals that are thermodynamically more stable. The reason behind these differences probably stems from the increased molecular diffusion expected for polymer macrocycles.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Parameters extracted from the Avrami fit to the data presented in Figure 2 for cyclic and linear PCL samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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