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Crystallization of Cyclic Polymers: Synthesis and Crystallization Behavior of High Molecular Weight Cyclic Poly(ε-caprolactone)s

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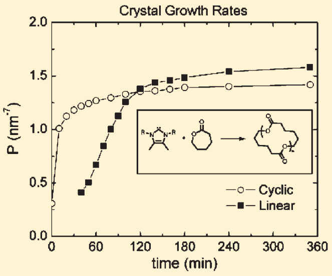
S Supporting Information

ABSTRACT: High molecular weight poly(ε-caprolactone)s (PCL) were synthesized via zwitterionic polymerization of ε-caprolactone initiated with N-heterocyclic carbenes. Ring-opening polymerization of ε-caprolactone (1 M) with carbenes 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) or 1,3,4,5-tetramethylimidazol-2-ylidene (**3**) affords cyclic PCL with molecular weights up to M_n = 114 000 g/mol. Crystallization of the cyclic PCL was investigated by synchrotron small-angle X-ray scattering experiments and differential scanning calorimetry. High molecular weight cyclic poly(ε-caprolactone) crystallizes with a similar lamellar thickness and long period spacing as linear poly(ε-caprolactone), but the crystallization of cyclic poly(ε-caprolactone) is faster than that of linear poly(ε-caprolactone) for molecular weights greater than 75 000 g/mol. These results imply that the polymer topology does not have a significant influence on the crystal structure or morphology but can have a significant influence on the rate of crystallization from the melt.



INTRODUCTION

The influence of macromolecular architecture on polymer properties has stimulated the development of new synthetic methods for the generation of well-defined macromolecules.[1−9] Synthetic methods to create branched[3] and dendritic macromolecules[2,5,10] have proven critical to investigations on the influence of branching on macromolecular behavior.[11,12] Cyclic polymers constitute one of the simplest topological isomers of linear chains,[9,13] yet the simple topological constraint of connecting the ends of a large macromolecule influences the properties in ways that remain poorly understood.[14−18] One of the challenges in the study of cyclic macromolecules is the limited set of synthetic methods to prepare large macrocyclic chains.[19−22] The formidable entropic constraints of cyclizing large chains[23] have stimulated some creative solutions to generate cyclic polymers. The development of new classes of high-yielding coupling reactions[22,24−26] and clever strategies for end-to-end coupling using electrostatic self-assembly,[27,28] coupling at interfaces,[29] in micelles,[30] or on solid-supports[31,32] are representative strategies that have improved the classical methods for cyclizing linear chains at high dilution.[13,14,20,21] Ring expansion strategies,[19,33−36] which avoid the entropic penalty of bringing chain ends in close proximity, provide another powerful strategy for the synthesis of cyclic macromolecules.

Despite these advances, synthetic challenges remain, particularly for the generation of high molecular weight cyclic polymers where entanglements are expected to have a large influence on their viscoelastic properties.[18,37] Moreover, few methods are available for generating high molecular weight crystalline polymers with cyclic architectures.[27,38,39] Recent experimental results on the crystallization of low molecular weight cyclic polymers[27,38−41] reveal a range of behaviors: experiments on poly(tetrahydrofuran) (M_n = 5100 g/mol) suggested slower crystallization kinetics for rings[27] whereas the investigations on poly(oxyethylene) (M_n = 1500 g/mol) showed faster kinetics for rings.[41] Utilizing a new ring-expansion polymerization strategy based on the cyclic Ru carbenes, Bielawski and co-workers studied the crystallization of high molecular weight cyclic polyethylene ($M_w \sim 200$ kg/mol).[33] These studies revealed that the melting point of cyclic polyethylene (T_m = 132 °C) is slightly higher than that of linear counterparts (T_m = 130 °C), and the enthalpy of fusion is identical for both cyclic and linear samples.[33]

Herein we describe a zwitterionic polymerization strategy to generate high molecular weight cyclic poly(ε-caprolactones) (cPCL). The critical role of crystallization rates and crystalline morphology on the properties of thermoplastics motivate us to compare the crystallization kinetics, crystalline morphology, and crystalline properties of linear and cyclic polyesters. The low entanglement molecular weight of PCL and its ability to crystallize provide an opportunity to investigate the influence of the cyclic architecture on the crystallization behavior.

RESULTS AND DISCUSSION

The zwitterionic ring-opening polymerization[42−44] of lactones mediated by N-heterocyclic carbenes (NHC) provides an expedient strategy for generating cyclic polyesters.[45−48] The ring-opening polymerization of lactide occurs within minutes at

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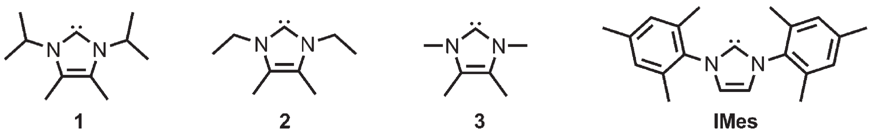

Figure 1. NHC's used for the zwitterionic ring-opening polymerization of lactones.

room temperature in the presence of 1,3-bis(2,4,6-(trimethylphenyl) imidazol-2-ylidene) (IMes) to generate cyclic poly(lactide)s (PLAs) with molecular weights in the range of M_w = 5000−26 000 g/mol.[45,47] As the entanglement molecular weight of linear PLAs is M_e = 8700 g/mol,[49] the cPLAs generated by this synthetic strategy are not highly entangled. Consequently, we sought to extend the zwitterionic polymerization to other monomers that might afford more highly entangled cyclic polyesters to investigate the influence of cyclic topology and molecular weight on the properties of crystalline cyclic polymers. Cyclic poly(ε-caprolactone) (cPCL) is an attractive target,[50] as it is a thermoplastic with a low T_m (~70 °C), a low glass transition temperature (T_g) of approximately −60 °C, and a relatively low M_e (~3 kg/mol for linear PCL).[51,52] We have previously shown that the aryl-substituted carbene IMes is inactive for the ring-opening polymerization of ε-caprolactone (CL), but alkyl-substituted carbenes such as 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) and 1,3,4,5-tetramethylimidazol-2-ylidene (**3**) yield linear PCLs in the presence of alcohol initiators.[53] We therefore investigated the zwitterionic ring-opening polymerization of CL in the absence of alcohol initiators in the presence of carbenes **1**, 1,3-diethyl-4,5-dimethylimidazol-2-ylidene **2**, and **3** (Figure 1).

The zwitterionic polymerizations of ε-caprolactone (CL) were performed in toluene or tetrahydrofuran (THF). In the absence of alcohol initiators, the carbenes **1**−**3** mediate the ring-opening polymerizations of CL at room temperature to produce high molecular weight cyclic PCLs with molecular weights ranging from M_n = 41 kg/mol to M_n = 114 kg/mol (Figure 2). The molecular weights of the PCLs obtained with carbenes **1**−**3** are considerably higher than the cyclic PLAs generated by IMes,[45,47] and the molecular weight distributions are broader, ranging from M_w/M_n = 1.36 (**2**, 33% conversion, entry 3, Table 1) to M_w/M_n = 2.16 (**2**, 74% conversion, entry 4, Table 1).

Evidence for a cyclic topology for the PCL's generated with carbenes **1**−**3** was provided by the absence of observed end groups in the ^{1}H NMR spectra and dilute viscosity measurements performed after purification by precipitation from methanol. A linear sample of PCL was prepared by the ring-opening polymerization of CL with $Et_2Al(OMe)$ (entry 2 of Table 2).[54,55] Comparison of the dilute solution viscosity of the linear PCL with that generated by the zwitterionic polymerization (entry 5 in Table 1) by gel permeation chromatography (GPC, THF) coupled with a light scattering detector and viscometer showed that the cyclic PCL exhibits a lower intrinsic viscosity than that of the linear PCL of similar molecular weight, consistent with a cyclic architecture (Figure 3).[56] The ratio $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$ = 0.72 ± 0.02 for molecular weights between 63 and 114 kg/mol. This ratio deviates from the theoretically predicted value for $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$ of 0.66, assuming an infinitely freely jointed chain at θ conditions, but as discussed by Goddard, the ratio of $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$ can vary from 0.71 to 0.64, depending on the degree the solvation of the chains.[57] Thus, the dilute viscosity measurements provide compelling evidence for a cyclic architecture, although we cannot rule out the presence of minor amounts of linear impurities.[58]

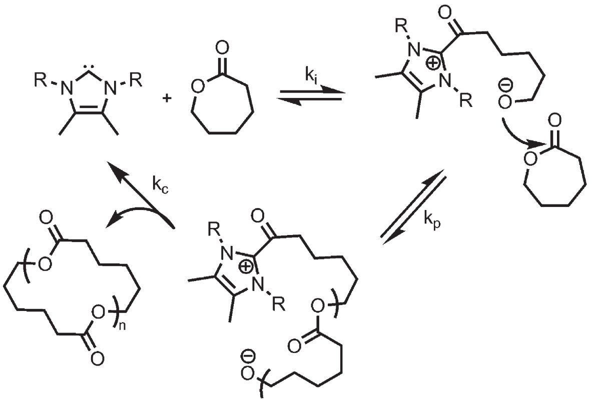

Figure 2. Proposed mechanism for the zwitterionic ring-opening polymerization of CL.

Table 1. Selected Data for Zwitterionic Ring-Opening Polymerization of CL with NHCs[a]

entry	carbene	solvent	time (min)	conv (%)[b]	M_n (kg/mol)[c]	PDI[d]
1	**1**	THF	360	30	41	1.75
2	**1**	toluene	600	38	114	2.03
3	**2**	toluene	60	33	54	1.36
4	**2**	toluene	360	74	81	2.16
5	**3**	THF	20	40	101	2.02
6	**3**	THF	360	78	66	1.91
7	**3**	THF	390	80	79	1.83

[a] All reactions were done at an initial monomer concentration $[M]_0$ = 1.0 M and a monomer to initiator ratio M/I = 100. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Number-average molecular weight determined by gel permeation chromatography (GPC), calibrated with polystyrene standards. [d] Polydispersity index; determined by GPC, calibrated with polystyrene standards.

The zwitterionic ring-opening polymerization of CL provides a new synthetic route to the preparation of high molecular weight cyclic PCL. As these materials are crystalline, we sought to compare the crystallization behavior of linear and cyclic PCL to investigate the role of topology on the lamellar structure and crystallization kinetics. Of particular interest is the crystallization of highly entangled and topologically confined cyclic polymers because little is known regarding the influence of a cyclic topology on the crystallization of high molecular weight cyclic polymers.[27,38−40] Crystallization of low molecular weight cyclic alkanes have revealed a number of differences between the linear and cyclic congeners; these studies are mostly limited to molecular weights where the total extended chain lengths are commensurate with the lamellar thicknesses.[14,59−61]

Wide-angle X-ray scattering experiments of both linear (L75k, M_w = 75K) and cyclic PCL (C110k, M_w = 110K) revealed that

Table 2. Linear and Cyclic PCL Samples Analyzed by DSC by Isothermal Crystallization at T_c = 45 °C

entry	name[a]	M_n (kg/mol)[b]	M_w (kg/mol)[c]	PDI[d]	M_w(LS) (kg/mol)[e]	T_m (°C)	ΔH_m (J/g)	$t_{1/2}$ (min)[f]
1	L120k	168	217	1.29	116	62	50	34.8
2	L100k	140	216	1.54	101	62	56	31.2
3	L75k	103	142	1.38	75	61	61	11.4
4	C140k	114	232	2.03	142	63	54	26.8
5	C130k	101	204	2.02	129	63	54	18.9
6	C110k	79	145	1.83	109	60	57	14.0
7	C75k	66	126	1.91	75	61	56	12.1

[a] L and C stand for linear and cyclic, respectively, and the number is from the M_w of the sample. Entries 4−7 are entries 1, 5, 7, and 6 of Table 1. [b] Number-average molecular weight determined by GPC, calibrated with polystyrene standards. [c] Weight-average molecular weight determined by GPC, calibrated with polystyrene standards. [d] Polydispersity index; determined by GPC, calibrated with polystyrene standards. [e] Weight-average (absolute) molecular weight determined by GPC using light scattering. [f] Half-times of crystallization.

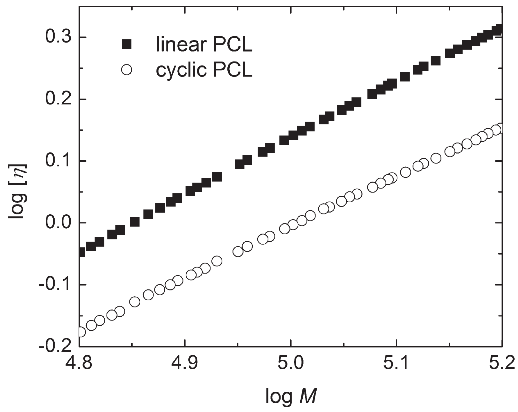

Figure 3. Mark−Houwink plots of the linear (■, entry 2 of Table 2, L100k) and cyclic PCL (○, entry 5 of Table 2, C130k) samples used for SAXS studies.

the powder patterns of both (2Θ = 21.31°, 21.44°; 22.00°, 22.01°; 23.61°, 23.72°; linear and cyclic, respectively) were very similar to each other and to that reported in the literature for linear PCL (2Θ = 21.2°, 21.8°, 23.6°; see Supporting Information).[62,63] This result suggests that cyclic PCL crystallizes and adopts a similar crystal structure to that of linear PCL.

Time-dependent SAXS measurements on the linear and cyclic samples were performed at the Stanford Synchrotron Radiation Laboratory (SSRL). Linear and cyclic PCL were isothermally crystallized at crystallization temperatures (T_cs) of 30, 35, 40, and 45 °C. The SAXS data obtained were analyzed under the assumption of the lamellar two-phase morphology. To derive structural parameters the long-period spacing (L_p) and lamellar thickness (L_c), the electron density correlation function $K(z)$[64] was derived from the SAXS curves by applying the Fourier transformation

$$K(z) = \frac{1}{2\pi^2 r_e^{\,2}} \int_0^\infty \left(\frac{\partial \Sigma}{\partial \Omega}\right)(q) q^2 \cos(qz)\, \mathrm{d}q \qquad (1)$$

where $(\partial\Sigma/\partial\Omega)(q)$ is the differential cross section per unit volume and r_e is the classical electron radius.

Shown in Figure 4 is the electron density correlation function, derived from the SAXS data, for linear and cyclic samples isothermally crystallized at 45 °C. From this plot, it can be seen that both the long-period spacing (L_p, ~20 nm) and lamellar thickness (L_c, ~9 nm) are very similar for the linear and cyclic PCL samples, suggesting that for these high molecular weight PCLs the lamellar spacing of the crystals is insensitive to the topology of the polymer (cyclic or linear) and is similar to that previously reported for linear PCL.[62] At these molecular weights, the lamellar thickness L_c is only a small fraction of the extended chain length of a cyclic PCL (~700 nm), implying that these cyclic PCLs are not only capable of undergoing multiple folds per lamella[39] but of spanning multiple lamellae. A further intriguing observation from the time-dependent SAXS experiments is that the cyclic PCL crystallizes faster than linear PCL during isothermal crystallization. An increase in the scattering intensity described by the invariant Q (i.e., $K(0)$)[65] for cyclic PCL is almost complete within 10 min, whereas the invariant Q of linear PCL gradually increases over the course of 120−350 min.

The Porod coefficient (P)[66] was determined as a function of time and used as a means to monitor the crystallization kinetics. The Porod coefficient is proportional to the interface area per unit volume (O_{ac}):

$$P = \frac{1}{8\pi^3} O_{ac} (\Delta\eta)^2 \qquad (2)$$

where $\Delta\eta$ denotes the difference in the electron densities of the lamellar and amorphous phases. Figure 5 illustrates that the cyclic PCL crystallizes faster than its linear counterpart at a crystallization temperature (T_c) of 45 °C. The same trend was found at other crystallization temperatures (T_c = 30, 35, and 40 °C).

The crystallization kinetics of a series of cyclic and linear PCL samples was further examined by DSC. A series of cyclic and linear PCL samples were prepared and studied to determine the effect of molecular weight on their crystallization behavior (Table 2). First, these samples were isothermally crystallized at 45 °C for a series of annealing times and then heated above their T_m to obtain ΔH_m by integration of the melting endotherm (see Supporting Information). The time dependence of the relative crystallinity (χ_c)[67] was monitored from the enthalpy of melting for a given annealing time t relative to the maximum enthalpy of melting achieved under experimental conditions. The relative crystallinities measured for the linear and cyclic samples as a function of time reveal that the cyclic PCL samples ($100 \le M_w \le 130$) crystallize more rapidly than the linear PCL samples at a crystallization temperature of 45 °C (Figure 6).

The linear form of the Avrami equation was employed to estimate the development of crystallinity as a function of annealing time:[68]

$$\ln(-\ln(1-\chi_t)) = n \ln(t) + \ln(k) \qquad (3)$$

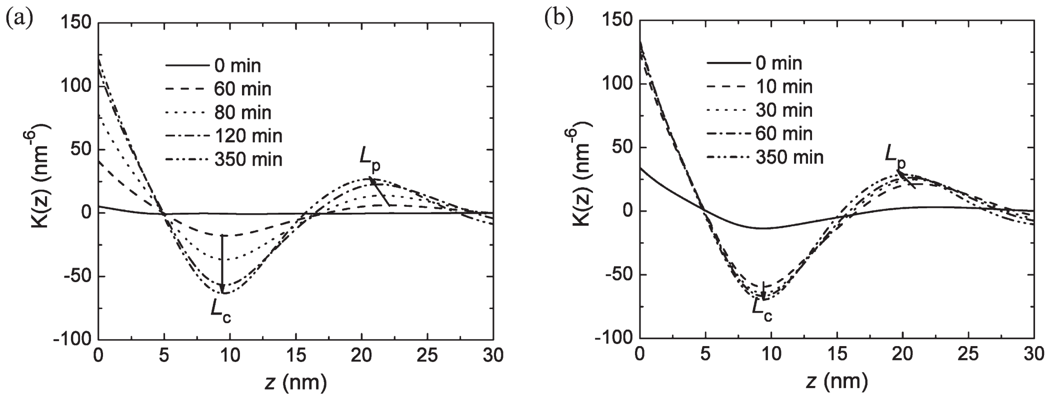

Figure 4. Electron density correlation function $K(z)$ for (a) linear PCL (L100k) and (b) cyclic PCL (C130k) versus time during isothermal crystallization at 45 °C.

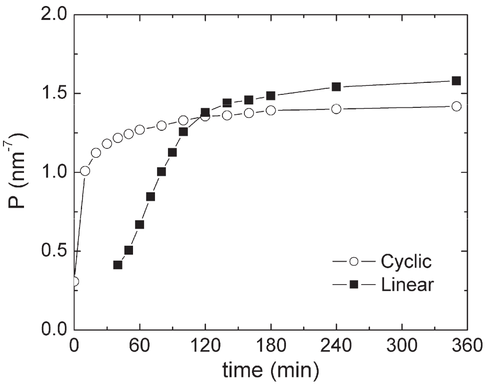

Figure 5. Crystal growth rates of cyclic (C130k) and linear (L100k) PCL during isothermal crystallization at 45 °C.

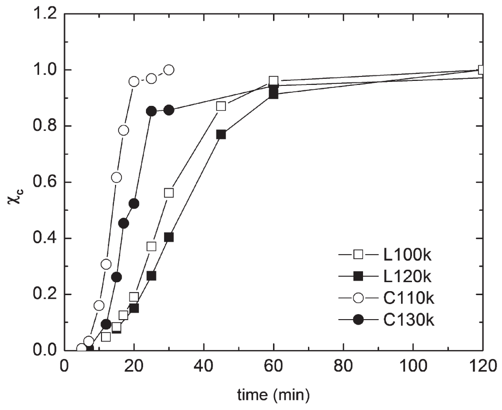

Figure 6. Relative crystallinity (χ_c) as a function of time for cyclic and linear PCL during isothermal crystallization at 45 °C.

The Avrami coefficient *k* and Avrami exponent *n* for the primary crystallization process for each polymer sample were estimated from the linear portion of the crystallization curve. (The linear form of the equation is inaccurate at high or low levels of crystallinity due to the difference in rates between the primary and secondary crystallization processes; see Supporting Information.) With this analysis, the half-life of crystallization $t_{1/2}$ could be estimated from *k* and *n* as follows:

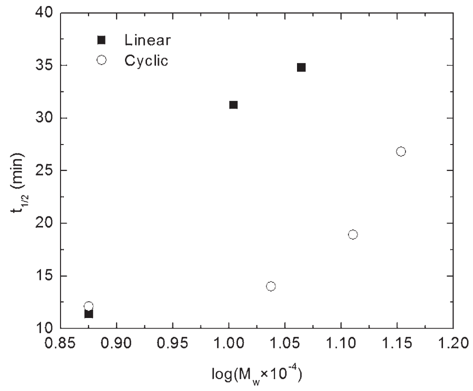

Figure 7. Half-times of crystallization as a function of M_w for cyclic and linear PCL crystallized isothermally at 45 °C.

$$k = \frac{\ln(2)}{{t_{1/2}}^n} \tag{4}$$

The $t_{1/2}$ of crystallization calculated for each polymer sample was evaluated as a function of molecular weight. As shown in Figure 7, high molecular weight cyclic PCL samples crystallize faster than linear PCL samples (as evidenced by smaller $t_{1/2}$ of crystallization), but lower molecular weight samples (M_w = 75K) exhibit similar crystallization kinetics.

The data from the time-dependent SAXS measurements and DSC analysis provide clear evidence that the high molecular weight cyclic PCLs crystallize faster than their linear congeners.[69] Given the paucity of data on the crystallization rates of high molecular weight cyclic polymers,[27,38−41] it is premature to draw conclusions about the generality of this observation. Our data at present do not allow us to draw firm conclusions as to the relative contributions of nucleation or growth, but the Porod analysis and DSC results imply that the growth rates are different for the linear and cyclic samples. As the crystallization kinetics are governed by both kinetic and thermodynamic factors, several possible origins can be proposed: (1) a lower melt viscosity for cyclic polymers in the melt[15,18,37] might lead to faster diffusion to the growing crystal front, (2) a higher equilibrium melting temperature (T_m°) for cyclic polymers might lead to larger supercooling ΔT ($\Delta T = T_m° - T_c$) for the cyclic

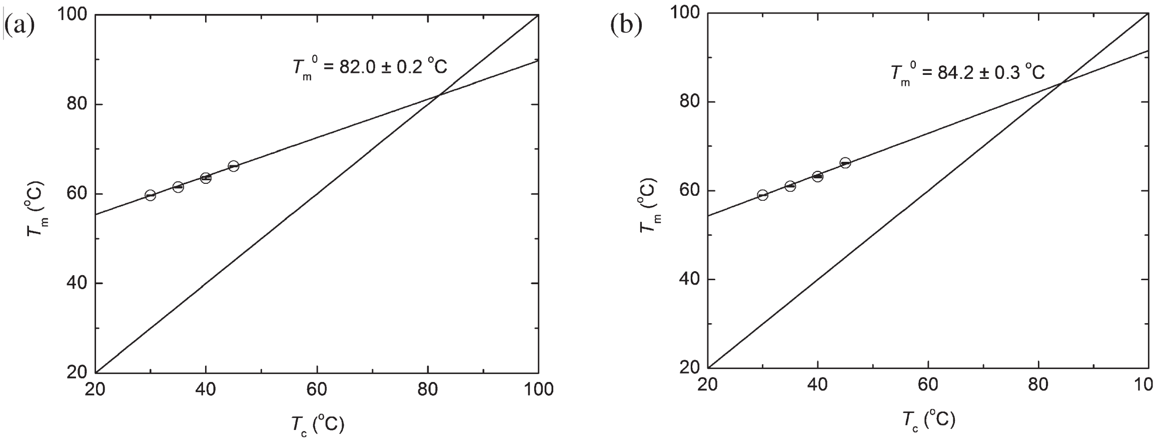

Figure 8. Hoffman–Weeks plots of (a) linear PCL (L120k) and (b) cyclic PCL (C110k).

polymers at a given crystallization temperature relative to the linear polymers,[33,39] and/or (3) the "collapsed" conformations proposed for cyclic polymers in the melt[17,70−74] might lead to lower kinetic barriers for crystallization.

As disentanglement from the melt is a critical feature of polymer crystallization,[66] differences in the entanglements between linear and cyclic PCL may be responsible for faster crystallization of the high molecular weight (M_w > 110 kg/mol) cyclic PCL samples. If the melt viscosities of the cyclic PCL are lower than that of the linear PCLs, as observed for other cyclic polymers,[15,18,37] then the high molecular weight cyclic polymers would be expected to crystallize faster. If disentanglement is a dominating influence of the crystallization kinetics, it is not obvious why the cyclic and linear samples of M_w = 75K crystallize at similar rates, as both the linear and cyclic samples should be highly entangled. It should be noted that the melt viscosity of cyclic polymers increase with even trace amounts of linear contaminants.[15,18,37,75] We cannot rule out the presence of small or variable amounts of linear contaminants in the samples we have investigated to date. The fact that the cyclic PCL samples of M_w > 110K crystallize faster than their linear analogues implies that for these samples the cyclic topology is the dominating influence on the crystallization kinetics, irrespective of possible contributions from trace amounts of linear polymers.

While kinetic factors are likely to dominate, we sought to assess whether there are fundamental thermodynamic differences between linear and cyclic chains that might contribute to their different crystallization rates. We carried out experiments to estimate the equilibrium melting point T_m^0 of the cyclic PCL samples. The equilibrium melting point (T_m^0) refers to the melting point of a crystal of infinite thickness and is a key thermodynamic parameter of the crystalline state.[66,76] As the crystallization rate is influenced by the degree of supercooling (ΔT) relative to T_m^0, the T_m^0 is fundamental to understanding the thermodynamic driving force for crystallization. The T_m^0 is defined as the transition temperature between the perfect amorphous and 100% crystalline phase, which is given by the ratio of the enthalpy of fusion (Δh^0) to the entropy of fusion (Δs^0)

$$T_m^0 = \frac{\Delta h^0}{\Delta s^0} \qquad (5)$$

If the enthalpy of fusion ΔH_f for both linear and cyclic polymers is assumed to be similar, then a higher T_m^0 would be predicted for cyclic polymers due to the lower configurational entropy of cyclic polymers in the melt (assuming the entropy of cyclic and linear polymers in the crystal is similar).[39] This is especially true if the configurations of high molecular weight cyclic polymers are "collapsed" in the melt.[17,70−74] Bielawski and co-workers proposed that the observed higher T_ms for cyclic polyethylene is due to the lower entropy of cyclic polymers in the melt.[33] To provide estimates of ΔTs for the linear and cyclic samples, DSC studies were carried out. T_m^0s for linear and cyclic PCL were estimated by extrapolating the melting point versus crystallization temperature (T_c) (Hoffman–Weeks plot).[76] As shown in Figure 8, this analysis indicates that the estimated T_m^0 for the cyclic PCL (T_m^0 = 84.2 ± 0.3 °C) is slightly higher than that of the linear PCL (T_m^0 = 82.0 ± 0.2 °C).

These data suggest that the T_m^0 of the cyclic PCL is higher than that of the linear polymer, but the difference is small (by this analysis). Strobl[66,77] has pointed out that the Hoffman–Weeks extrapolation underestimates T_m^0 ; the measurement of the lamellar thickness by SAXS provides a more direct measure of T_m^0.[66] Strobl reports a value of T_m^0 = 98 °C for linear PCL[77]—a value 20 °C higher than that estimated by the Hoffman–Weeks extrapolation of Figure 8. Time- and temperature-resolved SAXS studies were performed following the structure evolution during isothermal crystallization at T_c = 30, 35, 40, and 45 °C and subsequent heating to the melt. The extrapolated T_m^0 of linear PCL was found to be 97 °C, in good agreement with previous estimate of 98 °C reported for linear PCL (see Supporting Information). Unfortunately, we could not estimate the T_m^0 for the cyclic PCL as the slope of the crystallization line for the cyclic sample (T vs $1/L_c$) was larger than that of the linear sample and crystal thickening prevented an extrapolation to estimate T_m^0 (see Supporting Information). If the differences estimated by the Hoffman–Weeks analysis are representative of the true difference in T_m^0, then it is unlikely that this small difference is the origin of the faster rate of crystallization for the cyclic PCL.

■ SUMMARY

The zwitterionic ring-opening polymerization of ε-caprolactone provides a facile route to high molecular weight poly(ε-caprolactone). Comparisons of crystalline linear and cyclic PCL reveal that cyclic PCL displays the same lamellar thickness and long period as linear PCL, implying that high molecular weight cyclic PCLs undergo multiple folds per lamella and span multiple lamellae. Additionally, investigations by SAXS and DSC have shown that cyclic PCLs crystallize faster than their linear counterparts for molecular weight greater than 75 000 g/mol. This new synthetic method provides a unique opportunity to study fundamental questions about the role of polymer topology on bulk properties.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1–29.

(2) Grayson, S. M.; Frechet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819–3867.

(3) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.

(4) *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, NJ, 2002.

(5) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275–6540.

(6) Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309*, 1200–1205.

(7) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093–2107.

(8) Guan, Z. B. *Chem.—Asian J.* **2010**, *5*, 1058–1070.

(9) Tezuka, Y.; Oike, H. *J. Am. Chem. Soc.* **2001**, *123*, 11570–11576.

(10) Tomalia, D. A.; Frechet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719–2728.

(11) Kasehagen, L. J.; Macosko, C. W. *J. Rheol.* **1998**, *42*, 1303–1327.

(12) Kapnistos, M.; Semenov, A. N.; Vlassopoulos, D.; Roovers, J. *J. Chem. Phys.* **1999**, *111*, 1753–1759.

(13) Semlyen, J. A. *Cyclic Polymers*, 2nd ed.; Kluwer Academic Publishers: Dordrecht, 2000.

(14) Roovers, J. In *Cyclic Polymers*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordrecht, 2000; pp 347—384.

(15) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834–1852.

(16) Subramanian, G.; Shanbhag, S. *Phys. Rev. E* **2008**, *77*, 011801–011801—011809.

(17) Hur, K.; Winkler, R. G.; Yoon, D. Y. *Macromolecules* **2006**, *39*, 3975–3977.

(18) Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. *Nature Mater.* **2008**, *7*, 997–1002.

(19) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 251–284.

(20) Deffieux, A.; Borsali, R. In *Macromolecular Engineering. Precise Synthesis, Materials, Properties, Applications*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: Weinheim, 2007; pp 875—908.

(21) Endo, K. *New Front. Polym. Synth.* **2008**, *217*, 121–183.

(22) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009**, *38*, 2202–2213.

(23) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600–1606.

(24) Laurent, B. A.; Grayson, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 4238–4239.

(25) Stanford, M. J.; Pflughaupt, R. L.; Dove, A. P. *Macromolecules* **2010**, *43*, 6538–6541.

(26) Misaka, H.; Kakuchi, R.; Zhang, C. H.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 5091–5096.

(27) Tezuka, Y.; Ohtsuka, T.; Adachi, K.; Komiya, R.; Ohno, N.; Okui, N. *Macromol. Rapid Commun.* **2008**, *29*, 1237–1241.

(28) Tezuka, Y.; Mori, K.; Oike, H. *Macromolecules* **2002**, *35*, 5707–5711.

(29) Ishizu, K.; Ichimura, A. *Polymer* **1998**, *39*, 6555–6558.

(30) Ge, Z. S.; Zhou, Y. M.; Xu, J.; Liu, H. W.; Chen, D. Y.; Liu, S. Y. *J. Am. Chem. Soc.* **2009**, *131*, 1628–1629.

(31) Wood, B. R.; Hodge, P.; Semlyen, J. A. *Polymer* **1993**, *34*, 3052–3058.

(32) Chisholm, M. H.; Gallucci, J. C.; Yin, H. F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15315–15320.

(33) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041–2044.

(34) Xia, Y.; Boydston, A. J.; Yao, Y. F.; Kornfield, J. A.; Gorodetskaya, I. A.; Spiess, H. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 2670–2677.

(35) Boydston, A. J.; Holcombe, T. W.; Unruh, D. A.; Frechet, J. M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 5388–5389.

(36) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4723–4742.

(37) Roovers, J. *Macromolecules* **1988**, *21*, 1517–1521.

(38) Orrah, D. J.; Semlyen, J. A.; Dodgson, K.; Rossmurphy, S. B. *Polymer* **1987**, *28*, 985–990.

(39) Cooke, J.; Viras, K.; Yu, G. E.; Sun, T.; Yonemitsu, T.; Ryan, A. J.; Price, C.; Booth, C. *Macromolecules* **1998**, *31*, 3030–3039.

(40) Clarson, S. J.; Dodgson, K.; Semlyen, J. A. *Polymer* **1985**, *26*, 930–934.

(41) Nam, S. Ph.D. Dissertation, Georgia Institute of Technology, 2006 (http://etd.gatech.edu/theses/available/etd-11142006-11163351/).

(42) Johnston, D. S. *Adv. Polym. Sci.* **1982**, *42*, 51–106.

(43) Kricheldorf, H. R.; von Lossow, C.; Schwarz, G. *Macromolecules* **2005**, *38*, 5513–5518.

(44) Guo, L.; Zhang, D. *J. Am. Chem. Soc.* **2009**, *131*, 18072–18074.

(45) Culkin, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2627–2630.

(46) Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.

(47) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 4884–4891.

(48) Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *PMSE Prepr.* **2009**, *101*, 1154–1155.

(49) Dorgan, J. R.; Williams, J. S.; Lewis, D. N. *J. Rheol.* **1999**, *43*, 1141–1155.

(50) Hoskins, J. N.; Grayson, S. M. *Macromolecules* **2009**, *42*, 6406–6413.

(51) Gimenez, J.; Cassagnau, P.; Michel, A. *J. Rheol.* **2000**, *44*, 527–547.

(52) Ramkumar, D. H. S.; Bhattacharya, M. *Polym. Eng. Sci.* **1998**, *38*, 1426–1435.

(53) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42*, 1634–1639.

(54) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640–1646.

(55) Hofman, A.; Slomkowski, S.; Penczek, S. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 387–391.

(56) McKenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 498–512.

(57) Jang, S. S.; Cagin, T.; Goddard, W. A. *J. Chem. Phys.* **2003**, *119*, 1843–1854.

(58) For these high molecular weight samples, we cannot estimate with any precision the amount, if any, of linear impurities in these samples. Rheological studies[18] are underway as a means of estimating the purity of these samples.

(59) Drotloff, H.; Emeis, D.; Waldron, R. F.; Möller, M. *Polymer* **1987**, *28*, 1200–1206.

(60) Lieser, G.; Lee, K. S.; Wegner, G. *Colloid Polym. Sci.* **1988**, *266*, 419–428.

(61) Höcker, H.; Riebel, K. *Macromol. Chem. Phys.* **1977**, *178*, 3101–3106.

(62) Kohn, P.; Strobl, G. *Macromolecules* **2004**, *37*, 6823–6826.

(63) Li, S. M.; Pignol, M.; Gasc, F.; Vert, M. *Macromolecules* **2004**, *37*, 9798–9803.

(64) Roe, R. J. *Methods of X-ray and Neutron Scattering in Polymer Science*; Oxford University Press: New York, 2000.

(65) Porod, G. *Kolloid Z. Z. Polym.* **1951**, *124*, 83–114.

(66) Strobl, G. *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, 3rd ed.; Springer: Berlin, 2007.

(67) Jenkins, M. J.; Harrison, K. L. *Polym. Adv. Technol.* **2006**, *17*, 474–478.

(68) Schmidt, S. C.; Hillmyer, M. A. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 300–313.

(69) We have not carried out an exhaustive study of the crystallization kinetics as a function of the temperature of crystallization (T_c). However, experiments at $T_c = 40$ °C have been conducted and show the same trend; i.e., the cyclic sample crystallizes faster than the linear.

(70) Arrighi, V.; Gagliardi, S.; Dagger, A. C.; Semlyen, J. A.; Higgins, J. S.; Shenton, M. J. *Macromolecules* **2004**, *37*, 8057–8065.

(71) Cates, M. E.; Deutsch, J. M. *J. Phys. (Paris)* **1986**, *47*, 2121–2128.

(72) Iyer, B. V. S.; Lele, A. K. *Phys. Rev. E* **2006**, *74*, 021805.

(73) Obukhov, S. P.; Rubinstein, M.; Duke, T. *Phys. Rev. Lett.* **1994**, *73*, 1263–1266.

(74) Suzuki, J.; Takano, A.; Matsushita, Y. *J. Chem. Phys.* **2008**.

(75) Nam, S.; Leisen, J.; Breedveld, V.; Beckham, H. W. *Macromolecules* **2009**, *42*, 3121–3128.

(76) Gedde, U. W. *Polymer Physics*; Kluwer Academic Publishers: Dordrecht, 1999.

(77) Heck, B.; Hugel, T.; Lijima, M.; Sadiku, E.; Strobl, G. *New J. Phys.* **1999**, *1*, 17.11–17.29.