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Tin(II) Ethyl Hexanoate Catalyzed Precipitation Polymerization of ϵ-Caprolactone in Supercritical Carbon Dioxide

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ABSTRACT: The synthesis of biodegradable polyesters for biomedical applications in supercritical dioxide has been the subject of a number of recent publications. However, systematic studies of the mechanism of polymerization in this novel medium are rare. In this work, we present the first systematic study of the ring-opening polymerization of ϵ-caprolactone catalyzed by the industrially important catalyst tin(II) ethyl hexanoate. We report on the effects of varying reagent concentrations and conditions on the products obtained after polymerization in $scCO_2$ and compare this with the results obtained in conventional reaction media.

Introduction

Supercritical carbon dioxide ($scCO_2$) has attracted much recent attention as an environmentally friendly replacement for volatile organic solvents.[1,2] This novel reaction medium is nontoxic, inexpensive, and nonflammable, exhibits tunable properties, and has accessible critical parameters.[1−3] The high solubility of most monomers, combined with the poor solubility of most high molecular weight compounds, has led to the development of a number of heterogeneous polymerization processes in $scCO_2$, including precipitation, emulsion, suspension, and dispersion polymerizations, with free radical polymerization of vinyl monomers being the most intensely studied.[4−16]

In contrast to the large number of publications concerned with free radical polymerization, comparatively few deal with ring-opening polymerization (ROP). ROP is the most facile route to a number of linear aliphatic polyesters,[17−20] such as poly(caprolactone) (PCL), poly(L-lactide) (PLLA), and poly(glycolide) (PGA), all of which are biodegradable polymers with applications in the medical industry.[17,21−23] Hile and Pishko first reported the synthesis of poly(lactide-*co*-glycolide) in $scCO_2$[24] and went on to describe the development of an emulsion polymerization process in the presence of a $scCO_2$-soluble stabilizer.[25] Mingotaud and co-workers reported the ROP of ϵ-caprolactone (ϵ-CL) in $scCO_2$ in the presence of various initiators.[26−28] Our own group has reported the suspension polymerization of PLLA and PGA in the presence of both novel fluorinated[29] and hydrocarbon stabilizers[30] to produce biodegradable products as fine, easily processed powders in a one-step process. In addition, the enzyme-catalyzed ROP of ϵ-CL in $scCO_2$ has been reported.[31]

However, despite reports of a number of potential advantages for ROP in $scCO_2$ (i.e., the synthesis of biodegradable microparticles), very few systematic investigations of the mechanism and kinetics of ROP in $scCO_2$ have been reported. Stassin and co-workers recently published an investigation into the ROP of ϵ-CL $scCO_2$ initiated by dibutyltin dimethoxide (DBTDM),[32,33] but none have focused on the use of the most important ROP catalyst, the FDA approved tin(II) ethyl hexanoate ($Sn(Oct)_2$).[19,21,22] Detailed studies of ROP in supercritical chlorodifluoromethane have been recently published.[34,35]

This paper describes the first systematic investigation of the kinetics and mechanism of ROP catalyzed by $Sn(Oct)_2$ in $scCO_2$, using ϵ-CL initiated by butanol (BuOH) as a model system. The effect of modifying reagent concentration, temperature, and pressure is discussed in order to elucidate the effect of $scCO_2$ on ROP.

Experimental Section

Materials. ϵ-CL (99%) and BuOH (99%) were obtained from Aldrich, dried over CaH_2, and distilled before use. $Sn(Oct)_2$ (99%) was obtained from Aldrich and dried by azeotropic distillation with dry toluene, as described by Penczek and co-workers.[36] SCF grade CO_2 was obtained from BOC and used as received. All other solvents were obtained from Acros and used as received.

High-Pressure Reaction Vessels. The bulk of the reactions in this study were conducted in a clamp sealed autoclave equipped with an overhead magnetically coupled stirrer, as previously described.[29] Observations of phase behavior were conducted in a 100 mL view cell, also equipped with a magnetically coupled overhead stirrer and a sapphire window for viewing.

Size Exclusion Chromatography (SEC). Molecular weights and PDIs were obtained using chloroform as a mobile phase at 30 °C with a flow rate of 1 mL/min, using a LC1120 HPLC pump (Polymer Labs), a PL-ELS 1000 evaporative light scattering detector (Polymer Labs), and 2 × mixed “D” SEC columns (Polymer Labs). The system was calibrated against polystyrene narrow standards (Polymer Labs).

Method. ROP in $scCO_2$. The autoclave was first sealed and dried by heating to 120 °C and purging with SCF grade CO_2 for 1 h before use. The cell was then allowed to cool to the desired reaction temperature (80 °C) while purging continued. Unless otherwise stated, the polymerizations were conducted at 80 °C in order to mimic the conditions used in our previous studies. ϵ-CL (10 mL, 0.09 mols), BuOH (0.08 mL, 8.86×10^{-4} mol), and $Sn(Oct)_2$ (0.14 mL, 4.32×10^{-4} mol, $[CL]_0/[BuOH] = 2$, $[BuOH]/[Sn(Oct)_2] = 2$) were syringed into the autoclave through the pressure relief valve under a positive pressure of CO_2 to prevent contamination by atmospheric moisture. The reaction scheme can be found in Scheme 1.

The autoclave was then sealed, and the overhead stirrer switched on to 300 rpm. The autoclave was then pressurized to the desired reaction pressure (3500 psi, 250 bar, 25 MPa).

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Scheme 1. Sn(Oct)$_2$-Catalyzed ROP of ϵ-CL in ScCO$_2$

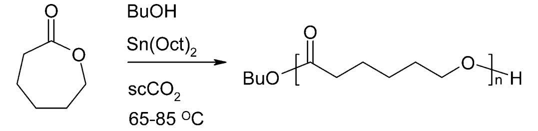

Table 1. Sn(Oct)$_2$-Catalyzed ROP of ϵ-CL in ScCO$_2$

sample^a	reaction time (min)	conv (%)^b	M_n^{c} (g/mol)	PDI^c
1	175	13.0	9 900	1.08
2	350	15.4	11 800	1.17
3	1110	58.2	44 600	1.35
4	1440	75.3	62 300	1.19
5	2165	84.6	67 400	1.18
6	3010	93.8	68 000	1.15

[a] PCL synthesized at 80 °C, 3500 psi, $[CL]/[I] = 103$, $[CL]_0 = 0.09$ mol, $Sn(Oct)_2 = 4.32 \times 10^{-4}$ mol, 300 rpm stirring. [b] Determined gravimetrically after precipitation into diethyl ether. [c] Determined via SEC vs PS standards.

During the reaction, the temperature was monitored by means of an internal thermocouple in contact with the reaction mixture. After 2165 min (approximately 36 h) the heater was switched off, and the vessel allowed to cool to room temperature. The vessel was then slowly vented to ambient pressure. To quantify conversion, the PCL product (a white solid) was dissolved by injecting 60 mL of chloroform into the autoclave through the pressure relief valve. This mixture was left to stir to ensure complete dissolution of the product. The vessel was then opened, and the contents were precipitated into a 4-fold excess of cold diethyl ether. The vessel was rinsed with a further 60 mL of chloroform to remove all traces of the product, and this was also precipitated into the same nonsolvent. While we appreciate that this is not exactly "green chemistry", it remained the most accurate method of determining conversion. The PCL product (a white solid) was isolated by vacuum filtration and dried overnight at 40 °C under reduced pressure. Conversion was then determined gravimetrically (8.46 g, 84.6% entry 5 Table 1).

ROP in Conventional Media. A two-neck 100 mL round-bottom flask equipped with a magnetic stirrer was flame-dried, stoppered with a rubber septum, and then immersed in a preheated bath of silicone oil at the appropriate temperature. Solvent (toluene or THF, if required) was introduced via a syringe, followed by the appropriate amounts of Sn(Oct)$_2$, BuOH, and ϵ-CL in the same order described in scCO$_2$. After preselected reaction times, the flask was removed from the oil bath and left to cool. After dissolution in chloroform (if required) the sample was precipitated into diethyl ether, isolated by filtration, and dried overnight at 40 °C under reduced pressure.

Results and Discussion

In the activated chain end mechanism of ROP (ACE-ROP) postulated by Penczek and co-workers,[36−41] the active species in the polymerization is a tin alkoxide species formed by Sn(Oct)$_2$ and an alcohol, in this case BuOH, as illustrated in Figure 1.

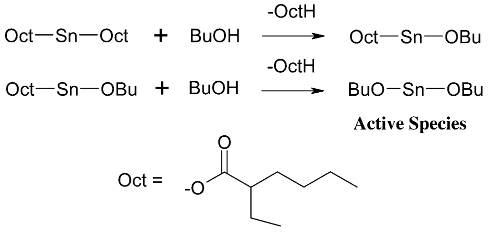

Figure 1. Reaction between Sn(Oct)$_2$ and BuOH, forming the active initiating alkoxide species.

The presence of both Sn(Oct)$_2$ and an alcohol is required to form the active species, and neither alcohol nor Sn(Oct)$_2$ is capable of catalyzing the reaction alone. The molecular weight of the product is controlled exclusively by the $[CL]_0/[BuOH]_0$ ratio, i.e., the M/I ratio. Increasing the ratio (i.e., decreasing the initial amount of BuOH) leads to an increase in molecular weight. Alcohol not consumed in the formation of the active species acts as a chain transfer agent, reducing the molecular weight. By contrast, the addition of excess Sn(Oct)$_2$ has little effect on the product molecular weight, as it requires the presence of an alcohol to form the required Sn−alkoxide bond.[36−41] Once all of the alcohol in the reaction is consumed, excess Sn(Oct)$_2$ has little effect upon the reaction. The ACE-ROP mechanism has been established as leading to a living polymerization;[42] i.e., no termination occurs throughout the course of the polymerization, and the product molecular weight increases in a linear fashion with conversion.

The solubility of each individual component reagent was examined qualitatively in a view cell equipped with a sapphire window before investigating the phase behavior of the entire reaction system. The view cell has a volume of 100 mL—larger than the conventional autoclaves (accurate volume including piping = 72 ± 2 mL). Consequently, the amount of each reagent placed in the vessel was raised to ensure the correct ratios of reagent to reactor volume and to replicate conditions used in a typical polymerization. For example, 10 mL of ϵ-CL in a 72 mL corresponds to a 13.8% loading; therefore, 13.8 mL was added to the 100 mL view cell. A temperature of 80 °C was chosen as the standard for polymerization conditions for this study, as it represented a compromise providing a reasonable rate of polymerization, but a low enough temperature to minimize transesterification. The cell was then heated to 80 °C, and liquid CO$_2$ was slowly added until the liquid contents dissolved (or to a maximum pressure of 4500 psi).

Under these conditions, it was found that BuOH was soluble in scCO$_2$ over nearly all pressures studied (the high solubility of BuOH in scCO$_2$ has been noted by other researchers).[43] Conversely, Sn(Oct)$_2$ (a liquid) was found to be largely insoluble in scCO$_2$ over the temperature and pressure range examined, forming a two-phase system at all times. It has been demonstrated previously that it is possible to impregnate Sn(Oct)$_2$ into ultrahigh molecular weight polyethylene disks using scCO$_2$.[44] This implies at least a limited level of solubility in the upper scCO$_2$ phase. However, those studies were conducted at higher temperatures compared to those under investigation here. In a separate experiment, a 2:1 molar mixture of BuOH/Sn(Oct)$_2$ was premixed and added to the view cell. This mixture also proved largely insoluble, forming a similar two-phase system under the conditions studied. This would imply that the tin alkoxide compound produced in the reaction between Sn(Oct)$_2$ and BuOH (see Figure 1) is also insoluble in pure scCO$_2$, although again this does not exclude the possibility of small amounts partitioning into the CO$_2$ phase.

ϵ-CL was found to be soluble in scCO$_2$ at 80 °C and a pressure of 2730 ± 100 psi (19.5 MPa) of CO$_2$, corresponding to a pure CO$_2$ density of 0.56 g/mL. On the basis of these results, a reaction pressure of 3500 psi (25 MPa, CO$_2$ density = 0.67 g/mL at 80 °C) was chosen as the standard pressure in this study to ensure that all polymerizations began in a single phase. It has been

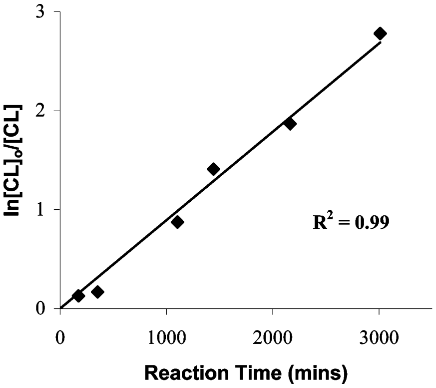

Figure 2. First-order kinetic plot for the Sn(Oct)$_2$-catalyzed ROP of ε-CL in scCO$_2$ ($k_{app} = 9.0 \times 10^{-4}$ min s^{-1}).

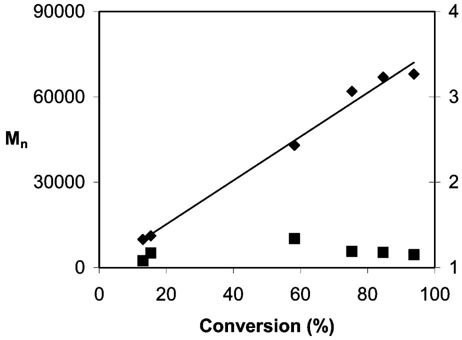

Figure 3. Evolution of M_n and PDI with conversion for the ROP of ε-CL in scCO$_2$. The diamonds refer to the evolution of M_n with conversion (right-hand axis) while the circles refer to the PDI of the product through out the reaction (left axis).

reported by Stassin and co-workers that a density of 0.6 g/mL was required to dissolve 15% v/v ε-CL in scCO$_2$,[32] a figure in good agreement with the one determined in this study.

When all the components were placed in the view cell at 80 °C and 3500 psi, the mixture was found to be soluble in the early stages of the reaction; a one-phase system was observed. It seems that ε-CL acts as a good cosolvent for the previously insoluble Sn(Oct)$_2$. After a relatively short time (around 10 min) the growing polymer could be seen precipitating out of solution and coalescing on the cell window. Therefore, it would appear that under these conditions the nature of the reaction is a precipitation polymerization.[45]

The next step was to probe the mechanism of the reaction and examine the influence of variables on ROP in scCO$_2$. To establish that Sn(Oct)$_2$ catalyzed ROP of ε-CL was controlled in scCO$_2$, we decided to investigate the influence of reaction time on the conversion and molecular weight of PCL. Table 1 shows the molecular weights and conversions obtained in scCO$_2$. Figure 2 shows the first-order kinetic plot for the Sn(Oct)$_2$ catalyzed ROP of ε-CL in scCO$_2$, while Figure 3 demonstrates the evolution of molecular weight with respect to conversion.

The linearity of the plot shown in Figure 2 leads to the conclusion that the reaction is first order with respect to ε-CL, as observed in conventional media.[36,41] In addition, the rate of reaction remains constant with reaction time, indicating a constant number of active sites throughout the polymerization. This implies a lack of termination in the system and indicates that the Sn(Oct)$_2$-catalyzed ROP of ε-CL is controlled (i.e., "living") in scCO$_2$. The pseudo-first-order rate constant (k_{app}) for the reaction under these conditions is found to be 9×10^{-4} min s^{-1}. A further indicator of controlled polymerization in scCO$_2$ is the linear evolution of molecular weight with conversion throughout the course of the reaction, along with a low value of PDI throughout (<1.5).

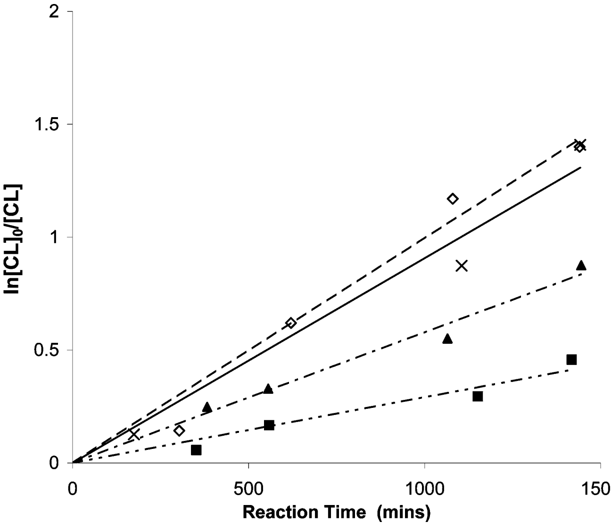

Figure 4. First-order kinetic plots to show the influence of [BuOH]$_0$ on the kinetics of ROP in scCO$_2$ (◇ = 0.16 mL of BuOH, $k_{app} = 1.0 \times 10^{-3}$ min s^{-1}, x = 0.08 mL of BuOH, $k_{app} = 9.0 \times 10^{-4}$ min s^{-1}, ▲ = 0.06 mL of BuOH, $k_{app} = 6.0 \times 10^{-4}$ min s^{-1}, ■ = 0.04 mL of BuOH, $k_{app} = 3.0 \times 10^{-4}$ min s^{-1}).

The influences of Sn(Oct)$_2$ and BuOH on the kinetics of ROP are a key feature of the mechanism. Increasing the initial concentration of both species results in an increase in the rate of polymerization, until the ratio of [BuOH]$_0$/[Sn(Oct)$_2$]$_0$, the initial quantities of reagents at $t = 0$, is equal to two (i.e., two molecules of BuOH for every one of Sn(Oct)$_2$). If the concentration of either species is increased above this ratio, then the rate of polymerization will plateau.[36,37,39,46,47] This is a result of the fact that both Sn(Oct)$_2$ and BuOH are required to form the active species, and after the complete consumption of either of the two species the additional molecules of Sn(Oct)$_2$ and BuOH are unable to react. Excess Sn(Oct)$_2$ simply spectates in the reaction, while excess BuOH acts as a chain transfer agent, resulting in a decrease in molecular weight but having no effect on the rate of polymerization.

To investigate the kinetics further, the measurements were repeated at a constant [Sn(Oct)$_2$]$_0$ while [BuOH]$_0$ was varied. In a similar manner, a new series of measurements were conducted where [BuOH]$_0$ was constant, and [Sn(Oct)$_2$]$_0$ was varied. The effects of these variations on the kinetics of ROP in scCO$_2$ in each case are shown in Figures 4 and 5, respectively, while the molecular weights and conversions obtained can be found in the Supporting Information.

Note that the linear first-order kinetic plots indicate the polymerization remains controlled under all of the conditions studied. The addition of excess BuOH (Figure 4) and Sn(Oct)$_2$ (Figure 5) results in an increase in the rate of polymerization and then a plateau when [BuOH]$_0$/[Sn(Oct)$_2$]$_0$ = 2. This again demonstrates that the ACE-ROP mechanism, postulated by Penczek and co-workers, is functioning in scCO$_2$ exactly as expected for both bulk and conventional solution polymerization.

The molecular weight of the product from ROP in conventional media is controlled exclusively by the ratio

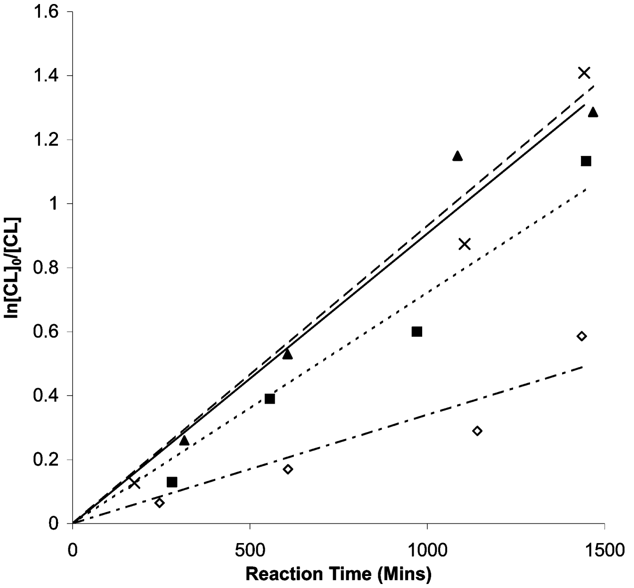

Figure 5. First-order kinetic plot to show the influence of $[Sn(Oct)_2]_0$ on the kinetics of ROP in $scCO_2$ (▲ = 0.18 mL of $Sn(Oct)_2$, $k_{app} = 9.0 \times 10^{-4}$ min s^{-1}, × = 0.14 mL of $Sn(Oct)_2$, $k_{app} = 9.0 \times 10^{-4}$ min s^{-1}, ■ = 0.10 mL of $Sn(Oct)_2$, $k_{app} = 7.0 \times 10^{-4}$ min^{-1}, ◇ = 0.07 mL of $Sn(Oct)_2$, $k_{app} = 4.0 \times 10^{-4}$ min s^{-1}).

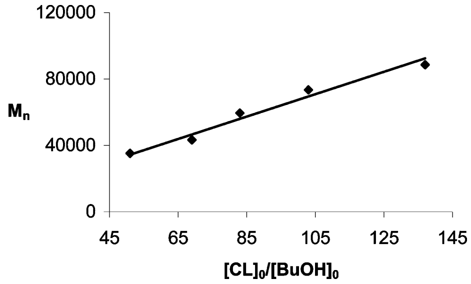

Figure 6. Influence of $[CL]_0/[BuOH]_0$ on the molecular weight of PCL synthesized in $scCO_2$. Note that product molecular weight is directly proportional to the M/I ratio.

of monomer to alcohol (i.e., M/I or $[CL]_0/[BuOH]_0$ ratio). BuOH will act as an initiator if sufficient $Sn(Oct)_2$ is present or as a chain transfer agent in excess concentration. By contrast, $Sn(Oct)_2$ cannot act as an initiator in the absence of BuOH or as a chain transfer agent in excess.[36,37,39,46,47] Consequently, the addition of BuOH lowers the final molecular weight of the product, while the addition of $Sn(Oct)_2$ has no effect. The influence of increasing the $[CL]_0/[BuOH]_0$ ratio and the effect of increasing $[Sn(Oct)_2]_0$ concentration is illustrated in Figures 6 and 7. Additional details can be found in the Supporting Information. Near quantitative yields were determined after precipitation in all cases, while the low PDI obtained indicates a controlled polymerization (see Supporting Information). Clearly, increasing the $[CL]_0/[BuOH]_0$ ratio (i.e., adding less BuOH) results in a higher overall product molecular weight, while the addition of excess $Sn(Oct)_2$ has little influence on the molecular weight of the PCL product. Both observations are indicative of the ACE-ROP mechanism occurring in $scCO_2$, as observed in conventional media.

Effect of Initial Pressure on ROP in $scCO_2$. To investigate the effect of pressure upon $scCO_2$-catalyzed ROP, the polymerization was carried out at a range of different initial pressures. In each case the reaction was terminated after 24 h and the conversion from each reaction compared after precipitation. The variation of conversion with reaction pressure is illustrated in Figure 8. Additional details can be found in the Supporting Information.

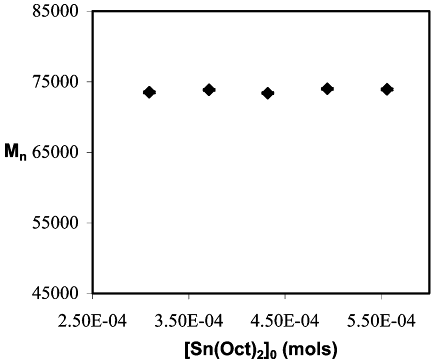

Figure 7. Influence of $Sn(Oct)_2$ on the molecular weight of PCL synthesized in $scCO_2$. Note that the concentration of $Sn(Oct)_2$ has almost no effect on molecular weight, as predicted from the ACE-ROP mechanism.

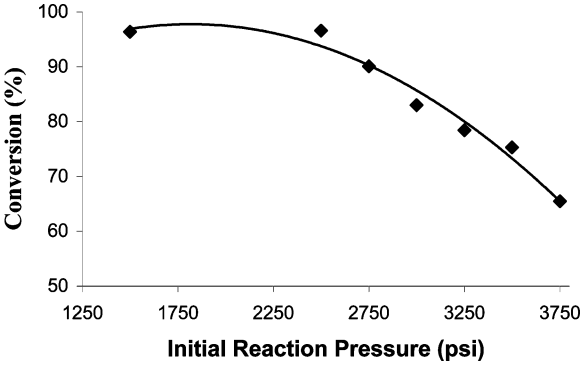

Figure 8. Influence of increasing initial reaction pressure on ROP in $scCO_2$. Note the reduction in conversion (and hence the rate of polymerization) at increasing pressure.

During each polymerization, the observed pressure of the reaction rose by between 300 and 500 psi. This is due to expulsion of CO_2 by the precipitated polymer and has been observed before by other researchers.[5,33,48] Figure 8 clearly shows that for a given reaction time the conversion of PCL decreases with increasing initial reaction pressure (and hence increasing initial CO_2 density). A similar trend was observed by Stassin and co-workers during their investigations with DBTDM[32] and indicates that the rate of polymerization is retarded with increasing CO_2 pressure. Together with the observation that the polymerization has a positive volume of activation in $scCO_2$, this was regarded as evidence that formation of a carbonate on the active chain end is responsible for a slower rate of ROP in $scCO_2$. This was subsequently confirmed after the observation of a tin carbonate species using FTIR.[32] On the basis of the results depicted above, it seems likely that a similar process is occurring in the case of $Sn(Oct)_2$, probably due to the fact that both reactions rely on similar active species.

Effect of Temperature on ROP in $scCO_2$. It is well-known that increasing the temperature of ROP results in an increase in the rate of polymerization in conventional media, and our next goal was to investigate the influence of temperature on $Sn(Oct)_2$-catalyzed ROP in $scCO_2$. A series of reactions were conducted at different reaction temperatures for 24 h, after which the reaction was terminated and the conversions calculated

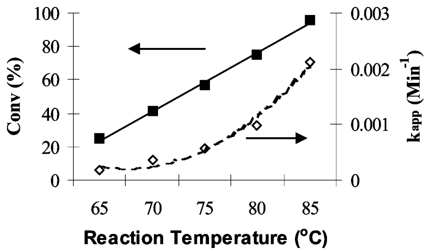

Figure 9. Influence of reaction temperature on conversion and k_{app} after 24 h reaction time in $scCO_2$. Note that increasing the temperature results in an increase in conversion and k_{app}.

Table 2. $Sn(Oct)_2$-Catalyzed ROP in Conventional Media

sample[a]	reaction medium	reaction time (min)	conv (%)[b]	M_n[c] (g/mol)	PDI[c]
1	bulk	30	8.0	4 000	1.10
2	bulk	40	13.6	12 000	1.15
3	bulk	55	19.8	14 000	1.14
4	bulk	85	36.9	28 000	1.15
5	bulk	115	54.2	38 000	1.30
6	bulk	150	67.2	56 000	1.40
7	bulk	190	79.1	61 000	1.28
8	toluene	210	20.6	17 000	1.10
9	toluene	1240	76.1	61 000	1.29
10	toluene	1720	84.6	65 000	1.30
11	toluene	2160	89.9	71 000	1.26
12	toluene	2740	94.9	73 000	1.28
13	THF	425	27.4	21 000	1.20
14	THF	1120	62.5	46 000	1.23
15	THF	1650	75.1	59 000	1.32
16	THF	2200	87.5	69 000	1.27
17	THF	2980	89.9	70 000	1.30

[a] PCL synthesized at 80 °C, in glassware using conventional techniques, $[CL]_0 = 0.09$ mol, $[CL]_0/[BuOH] = 103$, $[BuOH]/[Sn(Oct)_2] = 2$, 72 mL of solvent if required to mimic the conditions in the autoclave. [b] Determined after precipitation in diethyl ether. [c] Determined via SEC vs PS standards.

after precipitation. The effect of temperature is illustrated in Figure 9.

It can be seen that an increase in temperature results in an increase in the rate of polymerization of ε-CL in $scCO_2$. From these results, the activation energy for the reaction was determined via the Arrhenius equation from a plot of ln k_{app} vs $1/T$ (see Supporting Information). The activation energy was determined to be 89 kJ mol^{-1}, surprisingly close to the value obtained by Stassin and co-workers for the DBTDM initiated ROP of ε-CL in $scCO_2$.[32] It can be speculated that the active species in that case contains bonds of similar energy to the $Sn(Oct)_2$ system under investigation here, and thus the Sn−OBu active bond is also prone to competition from $scCO_2$.

Comparison of Kinetics of ROP in $scCO_2$ with Conventional Media. To further demonstrate that coordination of CO_2 onto $Sn(Oct)_2$ does indeed occur, the kinetics of the polymerization conducted in $scCO_2$ were compared to ROP conducted in conventional media under equivalent conditions. The kinetics of $Sn(Oct)_2$-catalyzed ROP were also investigated in THF, a polar coordinating solvent. The molecular weights and the conversions obtained can be seen in Table 2, while a comparison of the first-order kinetic plots can be seen in Figure 10.

In bulk reactions, the high local concentration of monomer to the active sites always results in a high rate of polymerization (see Figure 10).[45] ROP conducted in toluene is also faster than that conducted in $scCO_2$. This is consistent with previous studies and demonstrates that toluene, a noncoordinating solvent, does not adversely affect the rate of ROP. Stassin and co-workers found that polymerization in toluene was almost 50 times faster than that in $scCO_2$.[33] Here, we see a much smaller difference between the two rates (k_{app} measured in toluene is around 1.3 times larger than $scCO_2$). There are potentially several reasons for this. The concentration of ε-CL in toluene was higher than that in $scCO_2$ in Stassin's study, which would have resulted in an increase in the rate of polymerization. Second, that study was conducted at 40 °C, whereas 80 °C is used in this study owing to the lower reactivity of $Sn(Oct)_2$. It is possible that at higher temperatures the equilibrium governing the insertion of $scCO_2$ into the Sn−OR bond is more rapid, resulting in the chain end spending less time in the dormant carbonated state.

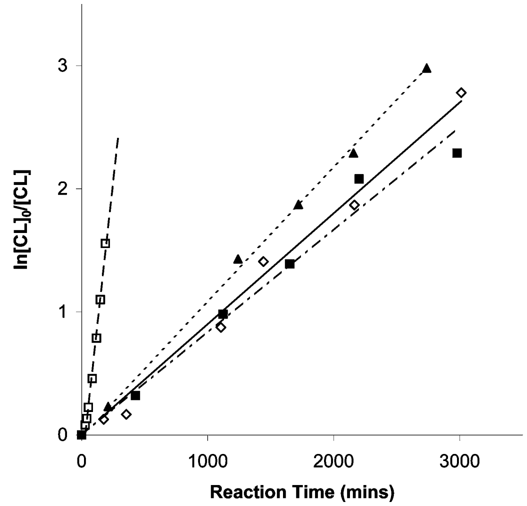

Figure 10. First-order kinetic plots showing the influence of reaction media on the rate of $Sn(Oct)_2$-catalyzed ROP. Note the similarity between the rate of reaction in $scCO_2$ and the rate of polymerization in THF (□ = bulk, $k_{app} = 9.2 \times 10^{-2}$ min s^{-1}, ▲ = toluene, $k_{app} = 1.1 \times 10^{-3}$ min s^{-1}, ◇ = $scCO_2$, $k_{app} = 9.0 \times 10^{-4}$ min s^{-1}, ■ = THF, $k_{app} = 8.0 \times 10^{-4}$ min s^{-1}).

Interestingly, there is very little difference between the rate of polymerization in THF compared to that in $scCO_2$. This was initially surprising, as at first glance there is little similarity between the two solvents. However, other researchers have also noticed a reduction in the rate of ROP in polar, coordinating solvents such as THF due to the solvent coordinating to the active metal center.[49,50] This is the first time that a polar coordinating solvent (THF) has been compared with a quadrupolar coordinating solvent ($scCO_2$) as a medium for ROP. The similarity between the two media does suggest that $scCO_2$ coordinating to the active chain end is responsible for the reduction in the rate of polymerization.

Conclusion

This study indicates that ROP of ε-CL catalyzed by $Sn(Oct)_2$ in $scCO_2$ proceeds via an identical mechanism to that which occurs in conventional media. This is evidenced by the effects of $Sn(Oct)_2$ and BuOH on the kinetics of the reaction in $scCO_2$ and the lack of influence of $Sn(Oct)_2$ on the molecular weight of the final PCL product. The polymerization is controlled, as shown by the linear evolution of molecular weight with conversion and the lack of termination during the polymerization. The molecular weight of the product can be controlled by the ratio of monomer to initiator, i.e., the $[CL]_0/[BuOH]_0$ ratio. Increasing the initial pressure of the reaction medium results in a decrease of the rate of polymerization, while increasing the temperature has the opposite effect and results in an increase in rate. The rate of ROP is generally retarded in $scCO_2$ compared to bulk or solution polymerization conducted in a noncoordinating solvent, such as toluene. The similarity of the rate of ROP in $scCO_2$ to that conducted in THF (a coordinating solvent) together with the similarity between the activation energy with a previous study suggests that the coordination of $scCO_2$ onto the active tin chain ends is responsible for this phenomenon. However, $Sn(Oct)_2$ has been shown to be an efficient and versatile catalyst for ROP in $scCO_2$.

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Supporting Information Available: Full conversions and product molecular weights for the influence of catalyst and initiator on kinetics, the influence of BuOH and $Sn(Oct)_2$ on molecular weight, the molecular weights obtained at different initial reaction pressures, the molecular weights obtained at different reaction temperatures, and the Arrhenius plot for the $Sn(Oct)_2$-catalyzed ROP of ϵ-CL in $scCO_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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