Macromolecules **2001,** *34,* 775−781 **775**

Ring-Opening Polymerization of ϵ-Caprolactone in Supercritical Carbon Dioxide

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Received July 18, 2000

ABSTRACT: The ring-opening polymerization of ϵ-caprolactone (CL) initiated by dibutyltin dimethoxide was studied in supercritical carbon dioxide at 40 °C, under a pressure of 210−215 bar. The polymerization is controlled as assessed by the linear dependence of $M_{n,SEC}$ on conversion and of $\ln([CL]_0/[CL])$ on time. Moreover, there is a good agreement between $M_{n,SEC}$ and $M_{n,calc}$, at least until 20 000 g/mol. The apparent rate constants of polymerization in different media increase as follows: sc CO_2, CFC-113, toluene, bulk. The kinetic order in initiator for the polymerization in solution and in sc CO_2 was extracted from the slope of $\ln k_{app}$ vs $\ln [Sn]_0$. It appears to depend on the initiator concentration in solution, which is not the case in sc CO_2.

Introduction

Over the past 10 years, environmental concern has prompted the scientific community to find ways to decrease the use of VOCs (volatile organic compounds). Supercritical carbon dioxide (sc CO_2) is an adequate reaction medium because of its low toxicity, low cost, and nonflammability.[1] Moreover, the availability of CO_2 as a byproduct of many industrial processes, its possible recycling, and easily accessible critical parameters ($P_c = 73.8$ bar/$T_c = 31.1$ °C) account for its steadily increased use.[2] Until now, however, most studies dealing with polymerizations in sc CO_2 are radical polymerization of vinylic monomers, such as methyl methacrylate and styrene.[1−3] Only a few works focused on ionic (cationic[4,5] and anionic[6,7]) and coordination-insertion polymerization.[8,9]

Poly(ϵ-caprolactone) (PCL) is one of the most attractive aliphatic polyesters for biomedical applications because of its biocompatibility and biodegradability[10] and for polymer blends because of its compatibility with a large range of polymers, such as poly(vinyl chloride), poly(styrene-*co*-acrylonitrile), nitrocellulose, poly(epichlorohydrin), and bisphenol A polycarbonate.[11] In coordination-insertion polymerization of ϵ-caprolactone (CL) promoted by tin alkoxides in solution and in bulk, the structure of the active species, the equilibria between them, and their contribution to propagation and side reactions (e.g., intra- and intermolecular transesterifications)[12,13] are known. However, nothing is known about the mechanism and the kinetics of heterogeneous ring-opening polymerization of CL in supercritical carbon dioxide.

This paper reports preliminary results about the ring-opening polymerization (ROP) of ϵ-caprolactone initiated by dialkyltin dialkoxides ($R_2Sn(OR')_2$) in supercritical carbon dioxide. This research may lead to a synthetic route to environmentally friendly polymers by a "green" technique. The use of dispersants to stabilize the growing PCL chains will be reported in a forthcoming paper.

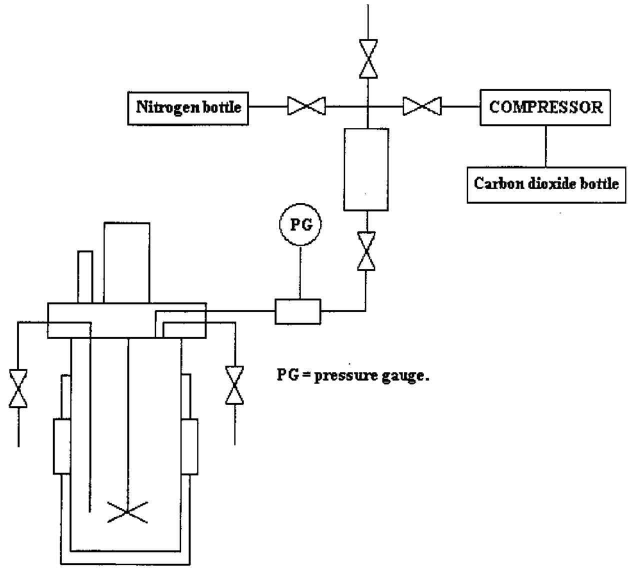

Figure 1. Scheme of the view cell used in this study.

Experimental Section

Materials. CL (Aldrich, 99%) was dried over CaH_2 at room temperature for 48 h and distilled under reduced pressure. Dibutyltin dimethoxide (Aldrich, 99%) was distilled under reduced pressure. Benzoyl chloride (Aldrich, 99%) (dried over calcium hydride) and triethylamine (Aldrich, 99.5%) (dried over potassium hydroxide pellets) were distilled prior to use. CFC-113 (1,1,2-trichlorotrifluoroethane, Aldrich, 99%) was dried over P_2O_5 and distilled prior to use. Toluene and tetrahydrofuran (LabScan, analytical grade) were dried by refluxing over the benzophenone−Na complex and distilled under nitrogen atmosphere just prior to use. Heptane and methanol (technical grade) were used as received. Carbon dioxide (analytical grade (N45); 7 ppm of water) was provided by "Air Liquide, Belgium" and used without further drying. $CDCl_3$ and CD_2Cl_2 (Aldrich, 99.5 atom % D) were used as received.

Polymerization Procedure in Supercritical Carbon Dioxide (Typical Example). The high-pressure reactor is schematized in Figure 1. Polymerization was conducted in a 130 mL stainless steel high-pressure cell equipped with two sapphire windows (Autoclave France), a magnetically coupled stirring system, and an electrical heating mantle. Pressure,

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10.1021/ma001252n CCC: \$20.00

Table 1. Polymerization of CL Initiated by $Bu_2Sn(OCH_3)_2$ in Supercritical Carbon Dioxide at 40 °C and 210−215 bar ($[CL]_0 = 1.39$ M)

entry	react time (h)	conv (%)	$M_{n,calc} \times 10^{-3}$ (g/mol)[a]	$M_{n,SEC} \times 10^{-3}$ (g/mol)	M_w/M_n	$[CL]_0/[Sn]_0$
1	0.25	28.0	1.40	1.00	1.25	88
2	0.57	41.8	2.10	1.50	1.25	88
3	0.83	61.4	3.00	2.60	1.25	88
4	1.17	48.5	4.50	4.00	1.25	167
5	2.00	71.0	6.50	6.60	1.40	167
6	2.75	80.0	8.40	7.40	1.50	167
7	1.50	38.0	5.40	5.00	1.30	254
8	2.50	53.8	7.60	6.70	1.45	254
9	3.83	69.0	9.80	10.0	2.00	254
10	1.60	25.5	5.00	5.10	1.30	364
11	2.67	52.0	11.4	10.5	1.45	364
12	5.00	72.0	15.0	14.5	1.65	364
13	7.00	80.0	16.1	16.1	2.05	364
14	9.75	92.0	21.6	18.5	1.85	364

[a] $M_{n,calc} = ([CL]_0/2[Sn]_0)M_{CL}(\text{conv}/100)$.

Table 2. Polymerization of CL Initiated by $Bu_2Sn(OCH_3)_2$ in Toluene at 40 °C ($[CL]_0 = 1.81$ M)

entry	react time (h)	conv (%)	$M_{n,calc} \times 10^{-3}$ (g/mol)[a]	$M_{n,SEC} \times 10^{-3}$ (g/mol)	M_w/M_n	$[CL]_0/[Sn]_0$
1	0.08	54.0	2.70	2.30	1.30	89
2	0.17	86.0	4.40	4.00	1.35	89
3	0.25	95.0	4.80	4.40	1.60	89
4	0.06	25.7	1.80	1.50	1.10	120
5	0.09	43.7	3.00	2.40	1.20	120
6	0.17	75.7	5.20	4.70	1.35	120
7	0.17	50.0	5.10	4.50	1.30	178
8	0.25	73.0	7.40	6.70	1.50	178
9	0.33	88.0	8.90	7.40	1.70	178
10	0.17	37.5	5.90	5.70	1.20	285
11	0.25	54.7	8.70	8.00	1.30	285
12	0.33	73.4	11.6	10.5	1.60	285
13	0.17	30.0	6.10	5.80	1.15	362
14	0.33	61.0	12.5	11.0	1.40	362
15	0.50	78.0	15.8	14.3	1.70	362
16	0.75	90.5	18.5	14.0	1.65	362
17	1.50	97.0	19.9	16.5	1.70	362
18	3.00	100.0	20.5	21.0	1.60	362

[a] $M_{n,calc} = ([CL]_0/2[Sn]_0)M_{CL}(\text{conv}/100)$.

Table 3. Polymerization of CL Initiated by $Bu_2Sn(OCH_3)_2$ in Bulk (Entries 1−4) and in CFC-113 (Entries 5−7) at 40 °C ($[CL]_0 = 9.0$ M (Entries 1−4), 1.81 M (Entries 5−7)/$[Sn]_0 = 2.5 \times 10^{-2}$ M (Entries 1−4), 5.0×10^{-3} M (Entries 5−7))

entry	react time (h)	conv (%)	$M_{n,calc} \times 10^{-3}$ (g/mol)[a]	$M_{n,SEC} \times 10^{-3}$ (g/mol)	M_w/M_n
1	0.10	29.5	6.00	5.50	1.20
2	0.17	70.0	14.3	11.9	1.60
3	0.25	81.0	16.5	15.3	1.80
4	0.33	100.0	20.5	21.0	1.80
5	0.17	15.2	3.10	3.30	1.40
6	0.50	42.9	8.80	7.30	2.00
7	1.00	58.8	12.0	10.7	2.15

[a] $M_{n,calc} = ([CL]_0/2[Sn]_0)M_{CL}(\text{conv}/100)$.

temperature, and stirring speed were monitored on a digital display control rack. Because of the sensitivity of dibutyltin dimethoxide toward humidity, the reactor was carefully cleaned and conditioned. The reactor was heated to 65 °C and purged with nitrogen for 15 min. While cooling to room temperature, it was evacuated for a few hours via a trap cooled by liquid nitrogen. Finally, it was purged with nitrogen for an additional 15 min. The initiator solution (1.0 mL of a 0.5 M solution in toluene; 5.0×10^{-4} mol of initiator) was added into the cell by a flame-dried syringe through an inlet port. The solvent (toluene) was removed under vacuum for a few minutes. CL (20 mL) was then added under a nitrogen flow by a flame-dried syringe. The reactor was then disconnected from the nitrogen line, evacuated, and connected to the carbon dioxide feed system. The cell was filled with liquid CO_2 to ca. 140 bar by an air-driven gas compressor (Maximator Schmidt Kranz & Co. GMBH) and then gradually heated to 40 °C to achieve a pressure of 210−215 bar. Polymerization was allowed to proceed for 9.75 h. The reactor was then cooled to 25 °C, and the CO_2 was vented through a needle valve into heptane in order to collect unreacted monomer. The polymer was collected as a coarse white powder. To quantify the CL conversion, the cell was rinsed with toluene in order to dissolve traces of polymer. This solution was poured into a large volume of cold heptane; the precipitated PCL was recovered by filtration and dried under vacuum at 40 °C overnight to constant weight. The monomer conversion was determined gravimetrically (92%). M_n was determined by SEC (21 600 g/mol).

Polymerization of CL in Solution, by Precipitation in CFC-113 and in Bulk (Typical Example). CL was polymerized in toluene, in CFC-113, and in bulk in a glass tube under stirring at 40 °C. The tube was equipped with a three-way stopcock, previously flame-dried, and purged with nitrogen. It was charged with 1 mL of a 0.05 M solution of dibutyltin dimethoxide in toluene (5.0×10^{-5} mol). In the case of bulk and precipitation (in CFC-113) polymerization, toluene was removed under vacuum. CL (2 mL, 0.0181 mol) and toluene (10 mL) or CFC-113 (10 mL) were added through rubber septa, using flame-dried stainless steel capillaries and syringes. Experiments with CFC-113 were conducted in sealed tubes. Polymerization reaction was left to proceed and stopped, after 3 h in toluene, 20 min in bulk and 1 h in CFC-113, by excess of a 1 M HCl solution. After dissolution in toluene (if necessary), the polymer was precipitated into an excess of cold heptane, recovered by filtration, and dried under vacuum at 40 °C up to constant weight. The monomer conversion was determined gravimetrically (100% in toluene and bulk, 59% in CFC-113). M_n was determined by SEC (see entry 18 in Table 2, entries 4 and 7 in Table 3).

Derivatization of the ω-Hydroxy End Group of Poly(ϵ-caprolactone). Hydroxyl end-capped poly(ϵ-caprolactone) ($M_{n,SEC} = 10^4$ g/mol, 10 g) was dried under vacuum at 40 °C overnight. It was added into a 250 mL one-neck flask equipped with a three-way stopcock and previously flame-dried and purged with nitrogen. Dried tetrahydrofuran (90 mL) was added through a rubber septum with a syringue, followed by dried triethylamine (2.8 mL; 2×10^{-2} mol) and benzoyl chloride (2.3 mL, 2×10^{-2} mol). The reaction was left to proceed at room temperature for 2 days. The cloudy solution was then filtrated in order to separate the insoluble ammonium salt and poured into cold methanol (1 L). The precipitated polymer was recovered by filtration. The polymer precipitation from THF into methanol was repeated twice. It was finally dried to constant weight and analyzed by ^1H NMR. The esterification of the end group was complete within the limits of experimental errors.

Polymer Characterization. Molecular weight and molecular weight distribution were determined by size exclusion chromatography (SEC) using a Waters 600 controller equipped with a Waters 610 fluid unit and a Waters 410 differential refractometer. A combination of three Waters Styragel columns with molecular weight ranges of 100−5000/500−30 000/5000−600 000 g/mol was used. The columns were eluted by THF (flow rate of 1 mL/min at 45 °C) and calibrated with polystyrene standards. The universal calibration curve was set up on the basis of the viscosimetric relationships for PS and PCL ($[\eta]_{PS} = 1.25 \times 10^{-4}M^{0.717}$, $[\eta]_{PCL} = 1.09 \times 10^{-3}M^{0.6}$). NMR spectra were recorded at 25 °C, using a Bruker AM 400 MHz spectrometer, in $CDCl_3$ for ^{13}C NMR and in $CDCl_3$ and CD_2Cl_2 for ^1H NMR. Chemical shifts were relative to TMS.

Results and Discussion

Mechanism and Kinetics of the CL Polymerization in Supercritical Carbon Dioxide. The ring-opening polymerization of CL initiated by tin alkoxides involves a coordination-insertion mechanism with selective cleavage of the acyl−oxygen bond of the monomer

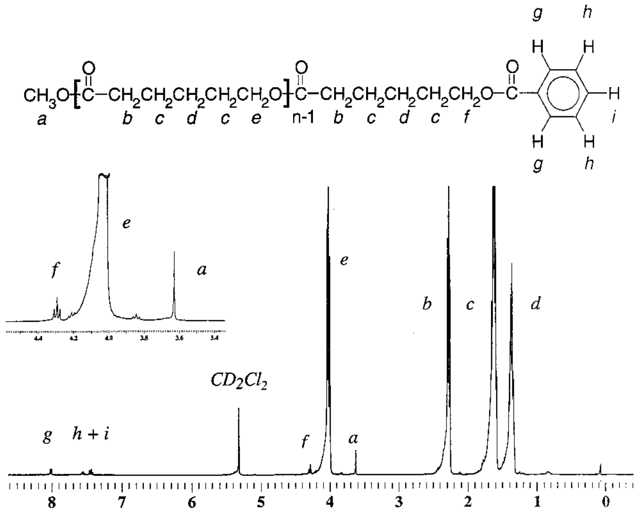
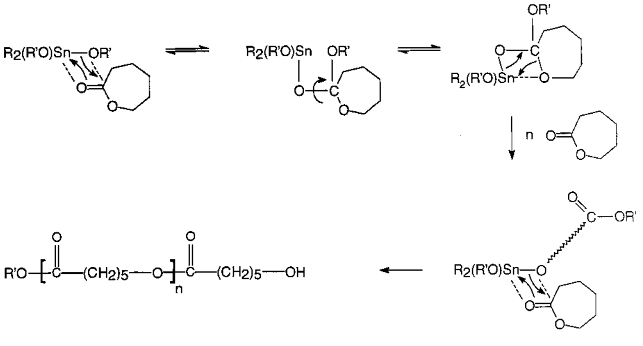


Figure 2. ^{1}H NMR spectrum of ω end-capped PCL in CD_2Cl_2.

Scheme 1



followed by insertion into the alkoxide−tin bond of the initiator[12] (Scheme 1, where R and R′ are alkyl groups). To confirm this mechanism, the end groups of the PCL chains were studied by ^{1}H NMR. The ratio of the intensities for the α-methyl end group and the ω-primary alcohol end group (I_α/I_ω) should be 1.5. The complexity of the ^{1}H NMR spectrum for the end groups is, however, a problem. Indeed, there is a complex peak at 3.60−3.70 ppm due to overlap of the singlet for the α-methyl ester and the triplet for the ω-primary alcohol. The I_α/I_ω ratio was approximated to 1.75 by deconvolution of this signal on the basis of Lorentzian functions. This value is close to 1.5 considering the limited accuracy of the method used. To improve the analysis of the end groups, the ω-hydroxyl group was esterified by benzoyl chloride. The ^{1}H NMR spectrum of the modified PCL was recorded in deuterated dichloromethane (Figure 2). Upon esterification of the $-CH_2OH$ ω end group, the resonance of the methylene protons is shifted downfield and observed as a triplet at 4.29 ppm. The α end group is observed as a singlet at 3.625 ppm. The experimental I_α/I_ω ratio (1.4) is in good agreement with the theoretical value of 1.5, which supports the mechanism proposed for the coordination-insertion polymerization of ϵ-caprolactone.

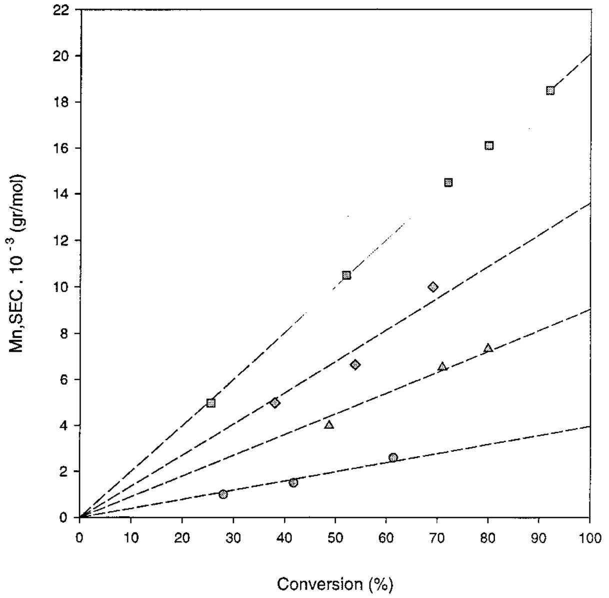


Figure 3. Dependence of $M_{n,SEC}$ on the monomer conversion (%) for the precipitation polymerization of ϵ-caprolactone (CL) initiated by dibutyltin dimethoxide in supercritical carbon dioxide at 40 °C and 210−215 bar. $[CL]_0 = 1.39$ M, $[CL]_0/[Sn]_0 = 364$ (square), 254 (diamond), 167 (triangle), and 88 (circle).

The ring-opening polymerization of CL was studied in a systematic way in supercritical carbon dioxide at 40 °C under a pressure ranging from 210 to 215 bar. Under these conditions of moderate temperature and high pressure, the density of the supercritical carbon dioxide is high enough (>0.75 kg/L) to solubilize the monomer. At the very beginning of the polymerization, the reaction medium is completely transparent, and the coexistence of two phases is not observed through the sapphire windows. Nevertheless, after a few minutes, the medium turns cloudy due to precipitation of the growing PCL chains. From Table 1 and Figure 3, it appears that the number-average molecular weight measured by SEC (universal calibration) increases linearly with monomer conversion, indicating that the number of reactive chains remains constant during polymerization. Moreover, the experimental $M_{n,SEC}$ depends linearly on the value calculated from the ratio of the monomer to initiator concentrations and the monomer conversion assuming that two alkoxide groups of dibutyltin dimethoxide initiate the ROP of CL. The correlation coefficient of the straight line shown in Figure 4 is 0.978 (slope = 0.911). The polymerization is therefore controlled, and M_n can be predicted from eq 1 (at least until 20 000 g/mol), where M_{CL} is the molecular weight of CL (114 g/mol), $[CL]_0$ is the initial monomer concentration, $[Sn]_0$ is the initial initiator concentration, and conv is the percentage of monomer converted.

$$M_n = ([CL]_0/2[Sn]_0)M_{CL}\cdot \mathrm{conv}/100 \qquad (1)$$

The molecular weight distribution (MWD), which is rather narrow at low monomer conversion, increases as the reaction progresses. This broadening of the MWD may be due to slow initiation compared to propagation and/or to intermolecular and intramolecular transesterification reactions typical of all tin-based systems.[12,13] Representative size exclusion chromatograms are shown in Figure 5. The peaks are quite symmetric although there is some tailing at high retention volumes, possibly due to the aforementioned transesterification reactions.

The kinetics of the precipitation polymerization of CL at 40 °C was investigated at a monomer concentration of 15 vol % compared to the cell volume and at several initiator concentrations, from 3.8 × 10^{-3} to 15.9 × 10^{-3} mol L^{-1}, which produces PCL with molecular weights ranging from 5000 to 20 700 g/mol. Figure 6 shows that the time dependence of $\ln([CL]_0/[CL])$ is linear, where

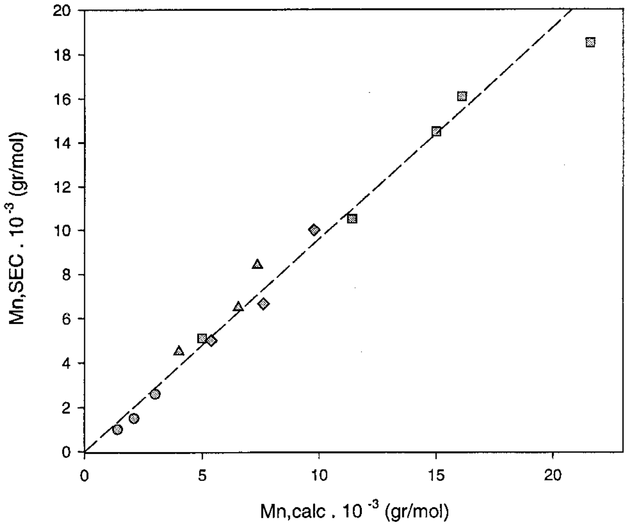


Figure 4. Plot of $M_{n,SEC}$ vs $M_{n,calc}$ for the precipitation polymerization of ϵ-caprolactone (CL) initiated by dibutyltin dimethoxide in supercritical carbon dioxide at 40 °C and 210–215 bar. $[CL]_0$ = 1.39 M, $[CL]_0/[Sn]_0$ = 364 (square), 254 (diamond), 167 (triangle), and 88 (circle).

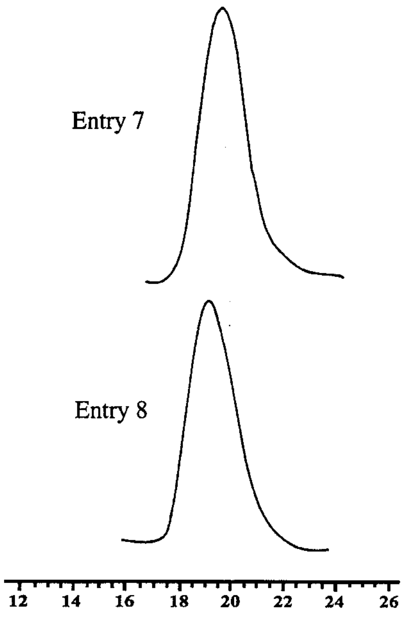


Figure 5. Size exclusion chromatograms for PCL formed in supercritical CO_2 (see Table 1).

$[CL]_0$ and [CL] are the monomer concentrations at time zero (t_0) and t, respectively. The first-order in monomer kinetics and the linear conversion dependence of the number-average molecular weight support a controlled coordination-insertion type of polymerization. Nevertheless, narrow molecular weight distribution samples were not collected as is the case when aluminum triisopropoxide is the initiator in apolar solvents at 0 °C.[14] The apparent polymerization rate constant was calculated from the linear regression of the data in Figure 6 using the equation $k_{app} = d(\ln[CL]_0/[CL])/dt$. The kinetic order in initiator (x) can be determined from eq 2.

$$-\frac{d[CL]}{dt} = k_{app}[CL] = k_{prop,app}[Sn]_0^x[CL] \qquad (2)$$

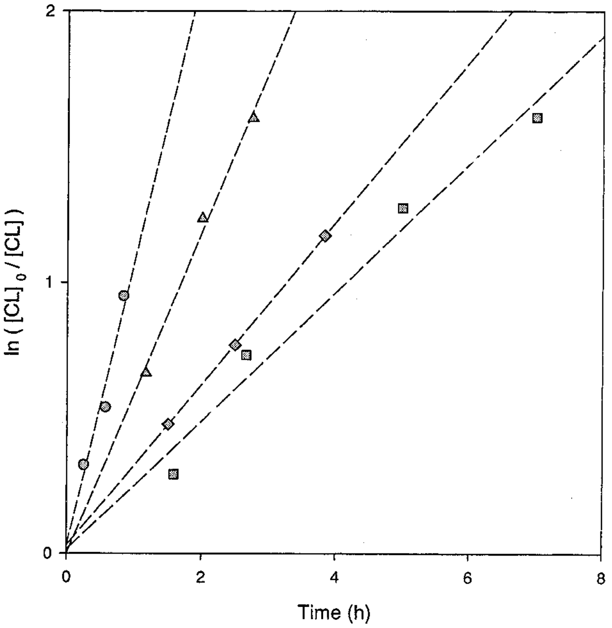


Figure 6. Kinetics of the ring-opening polymerization of ϵ-caprolactone (CL) initiated by dibutyltin dimethoxide in supercritical carbon dioxide at 40 °C and 210–215 bar. $[CL]_0$ = 1.39 M, $[CL]_0/[Sn]_0$ = 364 (square; $k_{app} = 3.95 \times 10^{-3}$ min^{-1}), 254 (diamond; $k_{app} = 5.00 \times 10^{-3}$ min^{-1}), 167 (triangle; $k_{app} = 9.90 \times 10^{-3}$ min^{-1}), and 88 (circle; $k_{app} = 18.0 \times 10^{-3}$ min^{-1}).

Metal alkoxides (initiators for the ROP of CL) predominantly exist as aggregates in equilibrium with nonaggregated species,[15] which may have completely different reactivity. For instance, only the nonaggregated dialkylaluminum alkoxides initiate and propagate the ROP of CL in contrast to the predominant aggregated species, which are inactive.[16] This specific situation can be schematized as follows.[15]

$$(P_n{}^*)_m \overset{K_{DA}}{\rightleftharpoons} m P_n{}^*$$

$$P_n{}^* + M \xrightarrow{k_{prop}} P^*_{n+1}$$

where P_n^*, $(P_n^*)_m$, and M are the nonaggregated species, the aggregated species, and the monomer, respectively. K_{DA} is the deaggregation equilibrium constant and m the degree of aggregation. Penczek et al. have proposed a method (eq 3) to determine the degree of aggregation from the plot of $\ln k_{app}$ vs $\ln [Sn]_0$ (the slope being equal to $1/m$, i.e., the order in initiator).[17]

$$k_{app} = k_{prop}[P_n{}^*] = k_{prop}(K_{DA}[(P_n{}^*)_m])^{1/m} \cong k_{prop}K_{DA}{}^{1/m}(1/m)^{1/m}[Sn]_0{}^{1/m}$$

$$k_{app} = k_{prop,app}[Sn]_0{}^{1/m} \Rightarrow \ln k_{app} = \ln k_{prop,app} + 1/m \ln [Sn]_0 \qquad (3)$$

This equation is valid for polymerization with a fast reversible aggregation of the active species. If the concentration of the active species is independent of the initiator concentration, the slope of the $\ln k_{app}$ vs $\ln [Sn]_0$ plot remains unchanged. A break is observed in the case of reversible aggregation (temporarily termination step) when the ratio of the aggregated and nonaggregated species changes.[18,19] Indeed, at low initiator concentration, aggregation is unfavored and m is small (if not 1). At high initiator concentration, aggregation dominates which increases m and decreases the slope of the $\ln k_{app}$ vs $\ln [Sn]_0$ plot. For ROP of CL initiated by diethylalu-

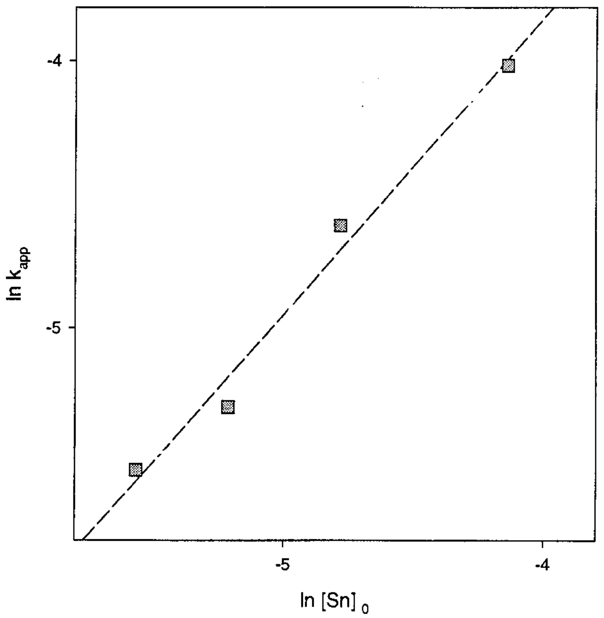


Figure 7. Plot of ln k_{app} vs ln $[Sn]_0$ for the ring-opening polymerization of ϵ-caprolactone (CL) initiated by dibutyltin dimethoxide in supercritical carbon dioxide at 40 °C and 210–215 bar. $[CL]_0 = 1.39$ M.

minum ethoxide at low concentration, the slope and the degree of aggregation are equal to one. At higher concentration, three molecules of this initiator aggregate, and the slope is accordingly $^1/_3$ and m is equal to 3.[16]

The apparent rate constants for the ring-opening polymerization conducted in sc CO_2 were calculated from the slope of the linear dependence of $\ln([CL]_0/[CL])$ vs time in Figure 6. These k_{app} values range from 3.95×10^{-3} min^{-1} at $[CL]_0/[Sn]_0 = 364$ up to 18×10^{-3} min^{-1} at $[CL]_0/[Sn]_0 = 88$. Figure 7 shows that ln k_{app} linearly depends on ln $[Sn]_0$, with a slope (kinetic order in initiator) close to 1 (1.11). Thus, the initiator is essentially unaggregated in sc CO_2 in the concentration range under consideration.

The CO_2 pressure changes during the polymerization. Because the volume contracts when CL is polymerized, the pressure should decrease with increasing monomer conversion. However, at low initial pressure such as 210–215 bar, the pressure increases with the polymerization progress, from 210 to 215 bar up to typically 235–240 bar, at high monomer conversion. DeSimone et al. reported the same phenomenon for the dispersion polymerization of styrene in sc CO_2.[20] These authors suggested that the thermodynamics of mixing favored the expulsion of CO_2 and monomer from the polymer phase at the low pressures used (ca. 200 bar).

Kinetics of the CL Polymerization in Solution in Toluene. To compare the polymerization kinetics in solution and in sc CO_2, kinetic data were collected in toluene at attempted molecular weights ranging from 5100 to 20 500 g/mol. For each CL/tin alkoxide molar ratio, $\ln([CL]_0/[CL])$ was plotted vs time. The dependence is quasi-linear with a correlation coefficient of at least 0.98, thus accounting for a kinetic order in monomer of 1. The collected data are listed in Table 2. The plot of ln k_{app} vs ln $[Sn]_0$ (Figure 8) shows that the kinetic order in initiator changes with concentration, which suggests that the aggregation degree changes. It is however quite unexpected to calculate a kinetic order higher than 1 (1.3) and thus a degree of aggregation smaller than 1 (0.77), at low initiator concentration. This type of observation has been reported very recently by Albertsson et al. in the case of dibutyltin cyclic dialkoxides[18] and by Penczek et al. for tin(II) dibutoxide.[19] According to Penczek et al., this phenomenon might indicate a higher reactivity of the aggregated tin alkoxide species compared to that of the nonaggregated species.[19]

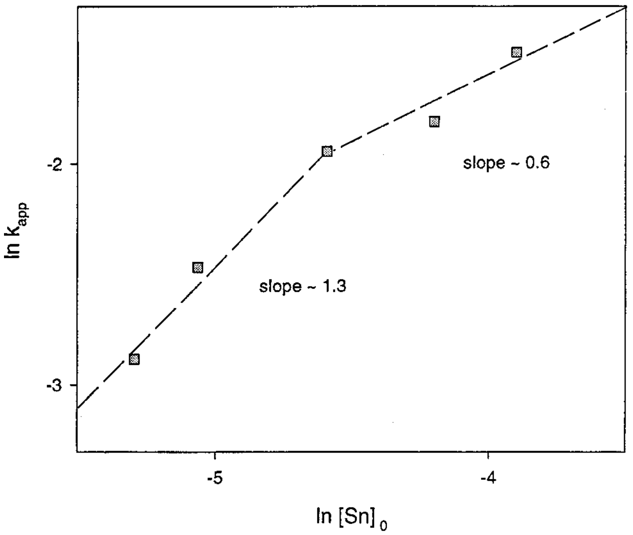


Figure 8. Plot of ln k_{app} vs ln $[Sn]_0$ for the ring-opening polymerization of ϵ-caprolactone (CL) initiated by dibutyltin dimethoxide in toluene at 40 °C. $[CL]_0 = 1.81$ M.

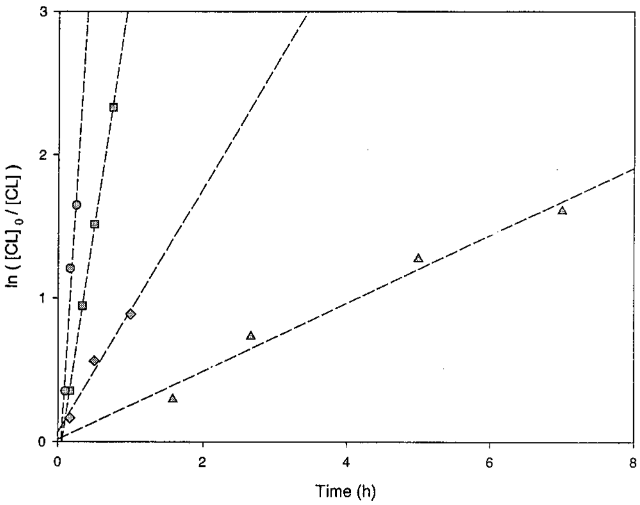


Figure 9. Kinetics of the ring-opening polymerization of CL in sc CO_2 (triangle; $[CL]_0 = 1.39$ M; $[Sn]_0 = 3.83 \times 10^{-3}$ M), in toluene (square; $[CL]_0 = 1.81$ M; $[Sn]_0 = 5.0 \times 10^{-3}$ M), in bulk (circle; $[CL]_0 = 9.0$ M; $[Sn]_0 = 2.5 \times 10^{-2}$ M), and in CFC-113 (diamond; $[CL]_0 = 1.81$ M; $[Sn]_0 = 5.0 \times 10^{-3}$ M) at 40 °C.

Comparison of ROP of CL in Supercritical CO_2, in Organic Solvent, in CFC-113 (Nonsolvent), and in Bulk. For the sake of comparison, the kinetics of the ring-opening polymerization of CL was studied in solution (toluene), in a nonsolvent (CFC-113), and in bulk, at 40 °C (Tables 2 and 3). In toluene and CFC-113, the monomer concentration (20 vol %) was slightly higher than in the high-pressure cell (15 vol %), the $[CL]_0/[Sn]_0$ molar ratio being ca. 360. Figure 9 compares the first-order kinetic plots for the ROP of CL in sc CO_2, in toluene, in CFC-113, and in bulk. The straight lines characteristic of the solution and bulk polymerizations have a much steeper slope than the straight lines

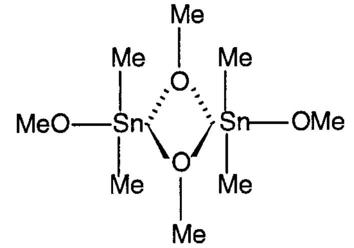


Figure 10. Structure of dimethyltin dimethoxide.

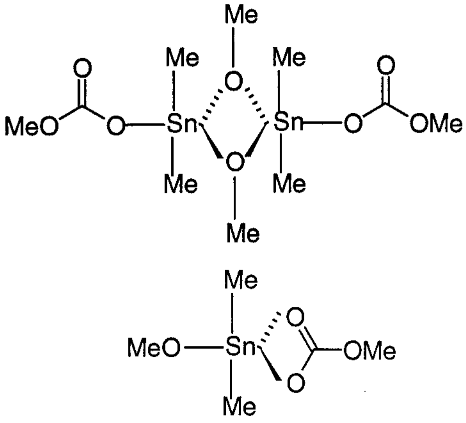
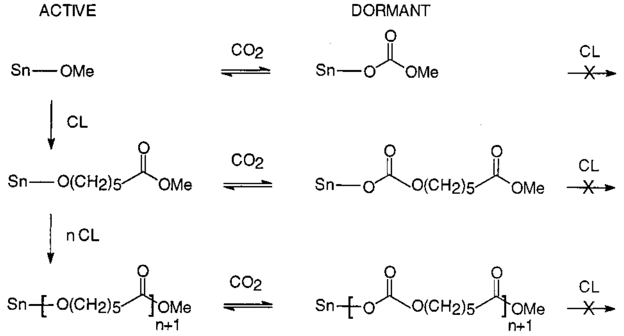


Figure 11. Structure of the complexes formed by dimethyltin dimethoxide with an excess of carbon dioxide.

observed for the precipitation ROP in CFC-113 and sc CO_2. The difference in the apparent rate constants is large. Indeed, k_{app} is 56×10^{-3} min^{-1} in solution, 130×10^{-3} min^{-1} in bulk, 15×10^{-3} min^{-1} in CFC-113, and 3.95×10^{-3} min^{-1} in sc CO_2. Therefore, on the basis of the k_{app} values, the polymerization at 40 °C is ca. 14 times faster in toluene and 33 times faster in bulk than in supercritical carbon dioxide. The value of k_{app} decreases from toluene to CFC-113, which suggests that the slower polymerization observed in sc CO_2 may also result from the polymer precipitation in this medium. A second reason could, however, be found in an interference of CO_2 in the polymerization process. Carbon dioxide and the ester carbonyl group of the monomer may compete for coordination onto the metal of the initiator which would slow the polymerization. According to Sakakura et al.,[21] dimethyltin dimethoxide (methoxo-bridged dinuclear species as shown in Figure 10) forms a complex with excess supercritical carbon dioxide, which consists of two types of methoxy groups as confirmed by ^{1}H and ^{13}C NMR analysis. ^{13}C NMR data agree with the insertion of CO_2 into one methoxy group per tin atom. ^{119}Sn NMR indicates a five-coordinated structure. The signal is however broadened at room temperature, consistent with a partial and rather slow dissociation process. Two kinds of carbonate complexes were postulated: a methoxo-bridged dinuclear complex (single crystals were collected but were unstable in solution at room temperature with release of CO_2) and a mononuclear complex (Figure 11). Therefore, the lower propagation rate constant in sc CO_2 may result from the formation of dormant species, i.e., carbonated tin−alkoxide species. To our best knowledge, tin−carbonate species have never been reported as active species in ROP of CL. Scheme 2 summarizes the main steps of a mechanism that is consistent with the experimental observations. In support of this tentative mechanism, ^{13}C NMR shows that no CO_2 is incorporated in the collected PCL samples. Indeed, one single peak characteristic of the ester carbonyl group is observed at 173.8 ppm. Work is in progress to confirm the mechanism and to improve the kinetics of the controlled ROP of CL in sc CO_2.

Scheme 2



Conclusions

ROP of ϵ-caprolactone was initiated in supercritical carbon dioxide by dibutyltin dimethoxide at 40 °C, under pressure of 210−215 bar, in the absence of dispersion agent. The molecular weight of PCL is controlled by the monomer/tin alkoxide molar ratio and the monomer conversion. The ROP is first order in both the monomer and initiator. The main criteria for a controlled ring-opening polymerization in sc CO_2 are thus fulfilled, which is reported for the first time. The increase in the molecular weight distribution with the monomer conversion indicates that transesterification reactions may occur, which precludes the livingness of the process. Competitive coordination of CO_2 onto tin may be the reason for a slower kinetics than in toluene and in bulk.

Acknowledgment. The authors are much indebted to the European Community for financial support (Brite Euram Project BE 97-4520 BRPR-CT97-0503) and to the “Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles” for general support to CERM in the frame of the “Pôles d'Attraction Interuniversitaires Polymères” (PAI 4/11). F. Stassin is grateful to FNRS (Belgium) for financial support in the frame of a research fellow grant.

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MA001252N