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Contribution of Supercritical CO_2 to the Preparation of Aliphatic Polyesters and Materials Thereof

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Summary: This paper is a short review of the most recent achievments of CERM in the synthesis of poly (ε-caprolactone) (PCL) and polylactides (PLA) in supercritical carbon dioxide (sc CO_2). In addition to the macromolecular engineering of these aliphatic polyesters, nanocomposites and PCL microspheres have been prepared with the assistance of this supercritical fluid.

Keywords: nanocomposites; polyesters; ring-opening polymerization; supercritical carbon dioxide; tin alkoxides

Introduction

Over the past decade, the environmental concern was rapidly growing, which explains the steadily increasing attention paid to materials produced by environmently friendly processes and/or biodegradable into benign byproducts. Nowadays, development of a sustainable technological platform for the production of biofriendly materials under environment-respectful conditions is thus a major target.

Among the actively studied "green" technologies, that one based on supercritical carbon dioxide (sc CO_2) is a central pillar of the existing portfolio. Supercritical carbon dioxide is a valuable reaction medium because of low toxicity, low cost, nonflammability and easily accessible critical parameters, which all account for a rapidly increasing use.[1] Polymerization in sc CO_2 has been considered in the recent past. When cyclic monomers are concerned, CO_2 is either a comonomer[2] or a reaction medium for the polymerization of, e.g., oxetanes, silicone precursors, oxazoline and cyclic (di)esters.[3-6] Cyclic (di)esters, such as ε-caprolactone, glycolide and lactides, are precursors of aliphatic polyesters,[7,8] known for biodegradability and biocompatibility.[9] The first examples of ring-opening polymerization (ROP) of cyclic (di)esters

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in compressed CO_2 date back to 1999 and were published by Mingotaud et al.[4] and Hile et al.[5] However, little information about the possible control of the polymerization was reported.

This paper aims at reviewing our recent effort in the preparation of aliphatic polyesters in sc CO_2, having in mind production of plain aliphatic polyesters, polyester-based nanocomposites and microspheres of poly(ε-caprolactone). Although not discussed here, sc CO_2 is also an efficient tool for the extraction of residual monomer and catalyst from the aliphatic polyesters, and for the preparation of microcellular materials.[10]

Results and Discussion

Polymerization of CL and LA in supercritical CO_2

The first method tested for the synthesis of aliphatic polyesters in sc CO_2 was the precipitation polymerization of ε-caprolactone (CL) initiated by tin octoate added with 2 equivalents of benzyl alcohol. This initiating system is not known for "livingness" and it is supposed to rely on the in situ formation of a tin alkoxide. It requires a temperature of 75°C or higher and long reaction times (beyond 10 – 15 h). In a first series of experiments, the high-pressure reactor was merely rinsed with an organic solvent and purged at room temperature with a compressed gas, followed by polymerization at 95°C under 200 bar, for at least 24 h. Under these conditions, no polymerization control was observed. In a second set of experiments, the reactor was thoroughly cleaned and dried, the temperature was decreased (75°C) and the pressure was increased (250 bar). Polymerization was fairly well controlled, polydispersity being rather low (Mw/Mn : 1.1 – 1.3) and molecular weight (Mn) reasonably close to the predicted value (Table 1).

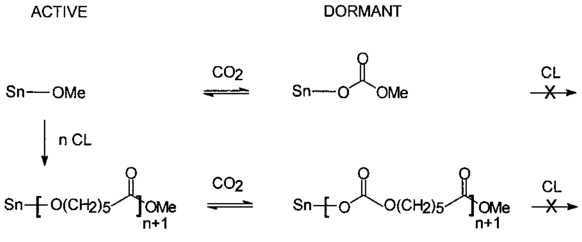
Table 1. Preparation of PCL in sc CO_2 by the tin octoate – benzylic alcohol system.

Entry	Mn theor. (K)	Mn SEC (K)	Time (h)	Conv. (%)	Mw / Mn
1 *	/	17.0	51	27	1.20
2	4.8	4.7	24	96	1.25
3	7.0	5.7	21	76	1.20
4	12.8	12.4	24	64	1.10
5	16.9	13.4	48	43	1.10
6	27.0	34.0	71	85	1.60

Experimental conditions : 20 % w/v of CL , 75 °C, 250 bar, dried reactor. SEC analysis with universal calibration. * No added benzylic alcohol

In our quest for controlled polymerization in sc CO_2, ROP of CL was also initiated by dibutyltin dimethoxide, at 40°C. The pressure of compressed CO_2 was 200-210 bar, and the CL concentration was 20 w/v %.[10] The ^{1}H NMR analysis of the chain–ends confirmed that ROP proceeds through the coordination-insertion mechanism, that commonly operates in organic solvents. Initially, the polymerization medium is transparent, consistent with the monomer solubility in CO_2 under the aforementioned conditions (density higher than 0.65 g/cm^3). A few minutes later, the medium turns cloudy as result of the PCL precipitation. Nevertheless, the experimental molecular weight increases regularly with conversion, and it is predetermined by the monomer-to-initiator molar ratio, at least until Mn = 20000 g/mol and on the assumption that two alkoxides per tin are active. Polymerization kinetics is first order in CL and first order in initiator, which indicates that tin species are basically non aggregated in supercritical CO_2. In contrast, whenever ROP is conducted in toluene, the kinetic order in initiator changes with concentration, a value of 1.3 being found at low initiator concentration. According to Penczek et al., a kinetic order higher than 1 would be the signature of an equilibrium between more reactive aggregated species and less reactive unaggregated species.[11]

For sake of comparison, the apparent rate constant for ROP of CL was measured at 40°C in different media: k_{app} is 56 x 10^{-3} min^{-1} in toluene, 130 x 10^{-3} min^{-1} in bulk, 15 x 10^{-3} min^{-1} in CFC-113 and 3.95 x 10^{-3} min^{-1} in supercritical CO_2. Thus ROP at 40°C is approximately 14 times faster in toluene and 33 times faster in bulk than in supercritical CO_2. This very slow kinetics in sc CO_2 has been explained by an equilibrium between propagating species and dormant species. The reversible insertion of CO_2 into the Sn-O bond results indeed in carbonated tin species inactive towards CL, as shown in Scheme 1. Formation of a carbonated chain-end was confirmed by infra-red spectroscopy (not shown here).



Scheme 1. Reversible carbonatation of propagating tin (IV) alkoxide by CO_2.

As far as pressure and temperature of polymerization in sc CO_2 are concerned, they have a strong effect on the reaction kinetics, as shown in Table 2. Indeed, at constant pressure, conversion increases with temperature, and at constant temperature, conversion decreases with pressure. From the experimental dependence of the polymerization rate constant on pressure and temperature, respectively, the Eyring theory of the activated complex and the Arrhenius law allowed the enthalpy, entropy and free energy of activation to be determined. These data are listed in Table 3 and compared for CL polymerization in sc CO_2 and toluene, respectively.[11]

Table 2. Effect of pressure and temperature on the kinetics of CL polymerization in sc CO_2 initiated by dibutyltin dimethoxide.

Temperature (°C)	Pressure (bar)	Conversion (%)	Mn,calc . 10^{-3} (g/mol)	Mn,SEC . 10^{-3} (g/mol)	k (sec^{-1}).10^{4}
40	120	44	6.6	6.9	1.610
40	200	36	5.4	5.9	1.240
40	250	31	4.7	4.6	1.030
40	200	36	5.4	5.9	1.240
50	200	78	11.7	12.4	4.205
60	200	95	14.3	14.3	8.320

When the activation energy is concerned, a value of 91 kJ/mol is reported for ROP in sc CO_2, i.e., approximately 50% higher than in toluene, which indicates a higher sensitivity of the polymerization kinetics to temperature, as is typically the case for chemical reactions with an inhibition step. The volume of activation for the CL polymerization is positive (90 cm^3/mol), in sharp contrast to commonly reported negative values for scCO_2-run polymerizations, e.g., radical polymerization. A positive activation volume is consistent with a carbonated chain-end, that has to expand and ultimately to release CO_2 for being active in polymerization. The CO_2 release from the activated complex explains why the activation entropy ($\Delta S^{\neq}$) in sc CO_2 is half the value determined for CL polymerization in toluene, at the same temperature (Table 3). Indeed, the negative contribution to entropy of the monomer coordination to the metal is partly compensated by the positive contribution of CO_2 release from the dormant carbonated polymer chain-ends.

Table 3. Parameters of activation for ROP of CL in sc CO_2.

Temperature (°C)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/(mol.K))	$\Delta G^{\neq}$ (kJ/mol)
40[a)]	90.2	- 32.1	100.2
40[b)]	62.9	- 64.9	83.3

[a)] ROP in sc CO_2 at 200 bar

[b)] ROP in toluene

There is thus a body of facts that supports the carbonation of the active species shown in scheme 1, as the reason for the slowing-down of the polymerization. At constant temperature, this effect is expected to be as strong as the initiator and the associated propagating species are reactive. This prediction is convincingly supported by aluminum triisopropoxide, which is a more reactive initiator than tin derivatives in ROP of CL. Indeed, only oligomers are then collected in sc CO_2, even after long polymerization time, which is not the case in toluene. As discussed below, an increase in temperature should be a way to tackle the deleterious kinetic effect of carbonation.

ROP of (L)-lactide (LA) was also carried out in sc CO_2, with dibutyltin dimethoxide as initiator. This polymerization is usually conducted at 70°C, thus above the melting temperature of the monomer. Figure 1 shows that the polymerization kinetics is basically the same whatever the solvent, i.e., sc CO_2 or toluene. Moreover, the molecular weight of PLA is controlled as shown in Figure 2. The experimental molecular weight is indeed in agreement with the value calculated from the monomer-to-initiator molar ratio and the actual monomer conversion (close to 100 %), and the polydispersity is moderately low ranging from 1.4 to about 1.7.

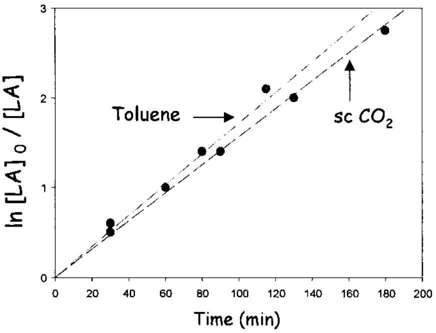


Figure 1. Kinetics of ROP of LA initiated by $Bu_2Sn(OMe)_2$ in sc CO_2 and toluene. $[LA]_0$= 1.4 M, $[LA]_0 / [Sn]_0$ = 140, T = 70°C, P = 290 bar.

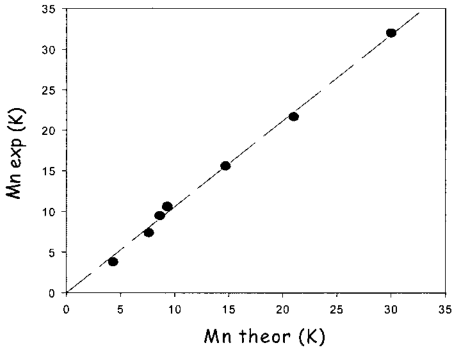
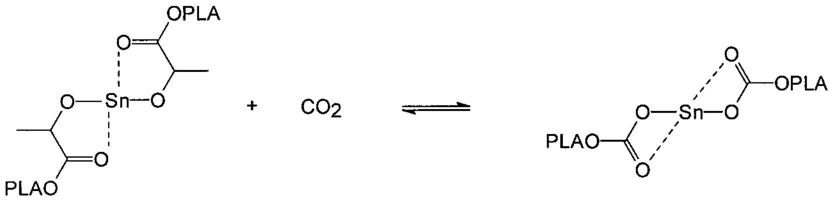


Figure 2. Dependence of experimental Mn (SEC with universal calibration) on the theoretical value for ROP of LA initiated by $Bu_2Sn(OMe)_2$ in supercritical CO_2. $[LA]_0$= 1.4M, $[LA]_0$ / $[Sn]_0$ = 140, T = 70°C, P = 290 bar.

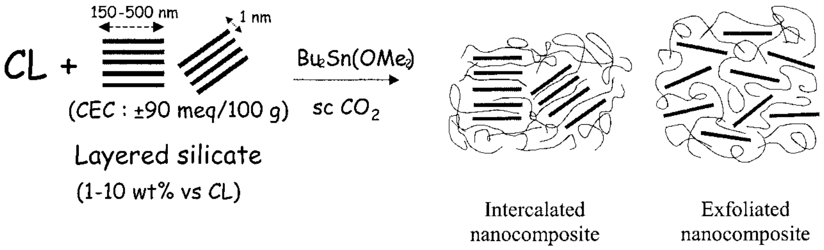
Three major reasons can explain the difference observed in the polymerization profiles of CL and LA in sc CO_2. First of all, because LA is insoluble in $scCO_2$, it must be heated above the melting temperature for being dispersed in the polymerization medium. At this higher temperature (70°C vs 40°C for CL), carbonation is no longer a favorable reaction, the carbonation-decarbonation equilibrium being shifted toward decarbonation. Secondly, the initiator is selectively dissolved in the monomer, which results in a higher concentration and thus in a faster reaction. Last but not least, the structure of the propagating tin alkoxide is such that tin can interact with the carbonyl of the penultimate LA unit with formation of a five-membered coordinated structure (Scheme 2). This intramolecular coordination competes the coordination insertion of CO_2 into the tin alkoxide bond, thus the formation of the dormant species.



Scheme 2. Sketch for the interaction of carbonated and uncarbonated PLA chains with tin.

PCL-based nanocomposites

Nowadays, much emphasis is laid on nanocomposites, which are nanoscopically reinforced materials with enhanced thermal, mechanical and barrier properties. All these properties can be imparted by the nanoscale dispersion of clay sheets into the polymeric matrix.[12] In addition to the straightforward but less efficient melt blending technique, nanocomposites can be prepared by polymerization in the presence of clay, either in solution or in bulk. Although more economically attractive, the implementation of the bulk approach is a problem because of the rapidly increasing melt viscosity. The use of sc CO_2 is again an effective way to solve this problem, because of the low viscosity and high diffusity of sc CO_2, together with the insolubility of PCL which can be recovered as a powder when CO_2 is released from the reactor. In addition to these advantages, a large amount of clay can be homogeneously and finely dispersed in sc CO_2, up to 50 wt% of CL.[13] Depending on the way the clay sheets are dispersed within the polymer matrix, two types of nanocomposites have to be distinguished, i.e., intercalated nanocomposites, in which the polymer chains are sandwiched in between the clay sheets and the exfoliated nanocomposites, in which the individual clay sheets are randomly dispersed (scheme 3).



Scheme 3. Polymer intercalation in the clay galleries vs. clay exfoliation.

Polymerization of CL was initiated by dibutyltin dimethoxide in the presence of montmorrilonite (MMT) previously made organophilic by the exchange of the native Na cations by long-chain alkylammonium cations, without (Cloisite 25A) or with hydroxyl end-groups (Cloisite 30B). The polyester chains are growing within the clay galleries as result of the monomer solubility in the highly diffusive sc CO_2. Representative data of this in-situ polymerization are collected in Table 4. There is a good agreement between experimental and theoretical molecular weights in case of Cloisite 25A (entries 3 and 4; Table 4). The hydroxyl groups attached to the alkyl ammonium cations in Cloisite 30B can initiate the CL polymerization by exchange with tin methoxide. Then, PCL chains are tethered at the surface of the clay sheets, which is favorable to their exfoliation. When the target molecular weight is high enough, less initiator is needed, and the impact of the alcohol-alkoxide exchange on the polymerization is then detectable (Mn_{exp} lower than Mn_{theor}, and higher polydispersity) (entries 1 and 2; Table 4).

Table 4. PCL nanocomposites prepared by ROP of CL initiated by dibutyltin dimethoxide in sc CO_2, in the presence of organomodified montmorillonites.

Entry	Mn theor. (K)	Mn SEC (K)	Time (h)	Conv. (%)	Mw / Mn
1(a)	17.8	15.0	24	85	1.65
2(b)	40.0	29.0	24	100	1.80
3(c)	11.3	13.1	24	70	1.60
4(d)	40.0	41.0	24	100	1.60
5(e)	15.0	14.7	36	95	1.70

[a] 4 wt % of Cloisite 30B (clay modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium), reaction at 50 °C and 190 bar.

[b] 3 wt % of Cloisite 30B, reaction at 50 °C and 165 bar.

[c] 5 wt % of Cloisite 25A (clay modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium), reaction at 50 °C and 190 bar.

[d] 3 wt % of Cloisite 25A, reaction at 50 °C and 165 bar.

[e] 50 wt% of Cloisite 25A, reaction at 55 °C and 165 bar.

As aforementioned, nanocomposites with a clay content as high as 50 wt% can be prepared very easily in sc CO_2 (entry 5; Table 4) compared to 10-20 wt% in case of bulk polymerization or polymerization in an organic solvent. Supercritical CO_2 thus opens the door to a unique technology for producing masterbatches of PCL nanocomposites, that can be dispersed in neat PCL or in any polymer miscible with PCL, including PVC, until the desired clay content is reached (usually a few wt%).

PCL nanocomposites were characterized by a series of techniques, i.e. transmission electron microscopy (TEM), X-ray diffraction (XRD), rheology and thermogravimetric analysis (TGA). As an example, the sample mentioned in Table 4, entry 1, was analyzed by XRD and rheology (Figure 3). The frequency dependence of the storage modulus is quite different for the nanocomposites compared to uncharged PCL. X-ray diffraction no longer shows the peak characteristic of the original clay, which supports that the clay is exfoliated.

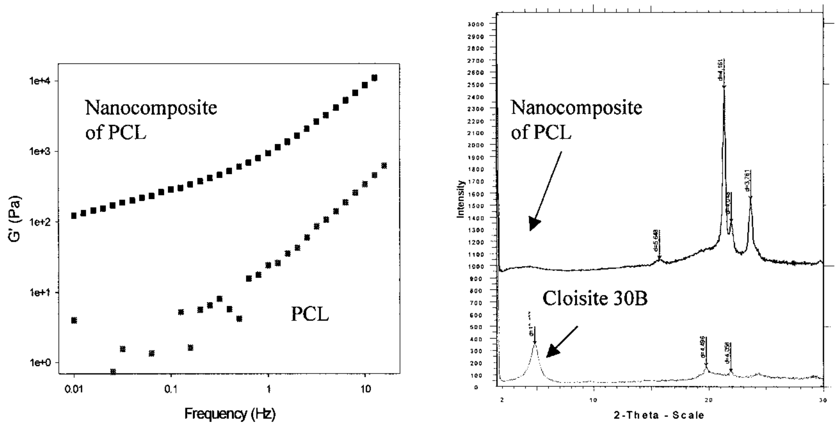
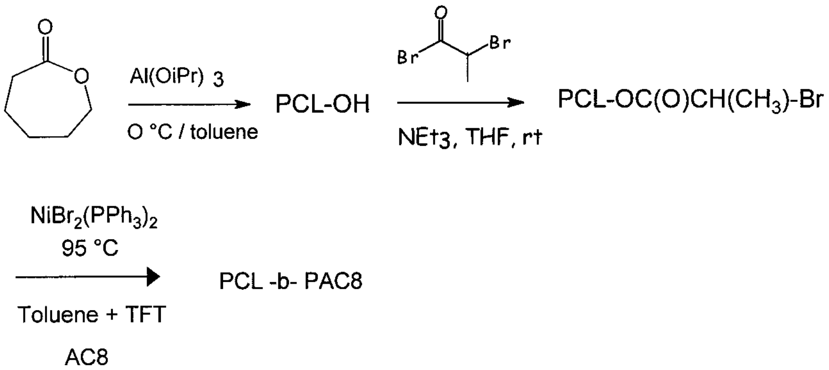


Figure 3. Dependence of G' (storage modulus) on shear frequency (left). X-ray diffractogram which supports clay exfoliation (right).

Production of PCL microspheres

Although the heterogeneous polymerization of CL leads to ill-defined pieces of solid polymer, microspheres can be prepared whenever the polymer precipitates in the presence of a few wt% of an on-purpose synthesized dispersing agent.[1] In this work, diblock copolymers consisting of a stabilizing CO_2-philic block, i.e., a fluorinated polyacrylate, and an anchoring PCL block, have been synthesized. These diblock copolymers were successfully prepared by the sequential controlled polymerization of CL and tetrahydroperfluorodecyl acrylate (AC8). ROP of CL was initiated by Al triisopropoxide, followed by derivatization of the PCL hydroxyl end-group into an activated bromide, which is the actual initiator for the atom transfer radical polymerization (ATRP) of the fluorinated acrylate (scheme 4). Because the two polymerization steps are well controlled, a series of well-defined copolymers were prepared with different molar compositions and/or total molecular weights.



Scheme 4. Sketch for the preparation of PCL-b-PAC8 diblock copolymers used in precipitation polymerization of CL in sc CO_2.

Solubility of the copolymer in sc CO_2 has been determined by the cloud point method and observed in the pressure range from 100 to 300 bar. As a rule, the monomer addition has a very beneficial effect on the solubility of the copolymers in sc CO_2.

Figure 4 illustrates the key effect that the copolymer composition has on the formation of PCL microspheres. Clearly, the relative length of the CO_2-philic block and the CO_2-phobic one must be optimized.

Figure 4 (left handside) shows that a too long CO_2-philic block (PAC8) compared to the anchoring block (24 K vs 5K) is detrimental to the adsorption and anchoring of the PCL block to the PCL particles. The average size of these particles is indeed in the 150-400 microns range. When the Mn(PAC8)/Mn(PCL) ratio is 2 instead of 5 in the previous example, the anchoring/solubility balance is much more favorable, and particles of a few microns are formed, as shown in figure 4 (right handside).

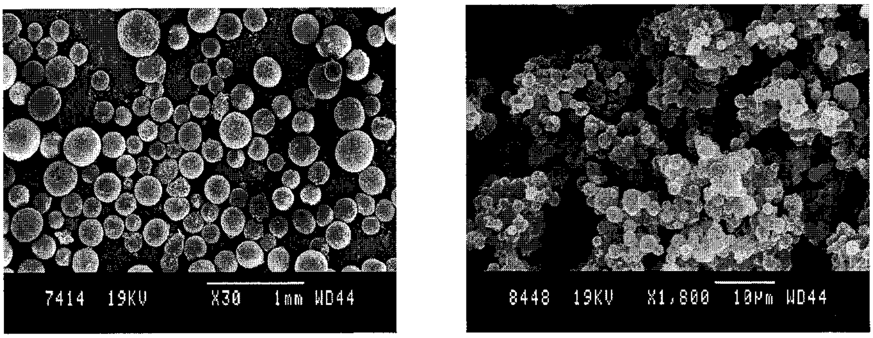


Figure 4. PCL particles prepared by ROP of CL in sc CO_2 in the presence of PCL(5K)-b-PAC8(24K) (left) and PCL(20K)-b-PAC8(40K), respectively. $[CL]_0$= 0.88 M, $[CL]_0$ / $[Sn]_0$ = 350, 5 wt% of surfactant vs CL, 40°C, 300 bar.

Conclusion

Sc CO_2 is a valuable alternative to the conventional organic solvents for the preparation of polyester-based materials. Precipitation polymerization of ε-caprolactone at 40°C and dispersion polymerization of (L)-lactide at 70°C are under control in sc CO_2. At 40°C, the tin alkoxide species that propagate the PCL chains are reversibly carbonated, which accounts for a slower polymerization than in toluene. This effect is no longer effective for the propagating PLA chains at 70°C. Supercritical CO_2 also contributes to extend the application range of the aliphatic polyesters, such as the production of highly-loaded PCL nanocomposites (up to 50 wt%) which are nothing but masterbatches to be dispersed in neat PCL and in any polymer miscible with PCL, such as PVC. PCL microspheres can also be prepared by using diblock copolymers with a properly balanced composition, as stabilizers for the precipitating PCL chains.

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