Effect of pressure and temperature upon tin alkoxide-promoted ring-opening polymerisation of ε-caprolactone in supercritical carbon dioxide

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Ring-opening polymerisation of ε-caprolactone in supercritical carbon dioxide is slowed down by a carbonation reaction, resulting in a positive volume of activation and a higher energy of activation as compared to polymerisation in a regular hydrocarbon solvent.

Recent years have witnessed intensive research effort into the use of supercritical carbon dioxide (sc CO₂) as a new reaction medium.[1–3] As far as polymerisation in sc CO₂ is concerned, most attention has been paid to the chain-growth polymerisation of vinyl monomers.[1-3] Ring-opening polymerisation (ROP) of cyclic (di)esters in sc CO₂ remained largely unexplored until 1999 when Mingotaud *et al.*[4] and Hile and Pishko[5] reported that ROP of various monomers could be carried out in sc CO₂. In 2001, our laboratory reported that the kinetics of ROP of ε-caprolactone (CL) were slowed down when conducted in sc CO₂ and proposed the carbonation of the active growing polymer chain-end into a dormant species as a tentative explanation.[6] Cyclic (di)esters, such as ε-caprolactone, glycolide and lactide are precursors of aliphatic polyesters, known for biodegradability and biocompatibility thus showing high potential for biomedical applications.[7–9] In this respect, production of these polymers under solvent-free conditions, such as in sc CO₂, combined with possible supercritical fluid extraction of residual monomer and initiator shows great promise. This communication aims at investigating further ROP of CL in sc CO₂ by the analysis of the parameters of activation for the polymerisation.

All the experiments were conducted in a monophasic regime, *i.e.* with CL completely soluble in the supercritical medium. For this purpose, solubility of CL in sc CO₂ was assessed by determining the cloud-point pressure at a constant concentration of CL ($[CL]_0 = 1.35$ M; *ca.* 15 vol%) and various temperatures. The solubilisation pressures were 90, 101, 132, 148 and 165 bar at 35, 40, 50, 55 and 60 °C, respectively. From these sets of values and the Peng–Robinson equation of state,[10] a critical density of CO₂ for dissolution of CL was calculated as *ca.* 0.6 g cm⁻³. It must be noted that precipitation ROP of CL in sc CO₂ is controlled, *i.e.* good agreement between experimental and theoretical molecular weight, in the range of temperature and pressure investigated in this work (Table 1). Polymerisation was carried out at 40 °C, under various pressures for one hour, according to a previously reported standard procedure.[6] Monomer conversion was measured and used to determine the apparent first-order rate constant (k) and the experimental error on k. The volume of activation of the reaction must be known to discuss the effect of pressure on the reaction kinetics. This volume is positive or negative, depending on whether increasing pressure is detrimental or not to polymerisation (see eqn. 1, valid for a first-order reaction).[11]

$$(\delta\ln k/\delta P)_T = -\Delta V^{\neq}/RT = -[V_{TS} - (V_{Polymer} + V_{CL})]/RT \tag{1}$$

The volume of activation can be expressed as the addition of two terms. One is related to the difference in the molecular size of the reagents in the original state and in the transition state (TS). The second term is related to the solvent–transition state interactions. It is positive, whenever the solvent shell is expanded by a reagent moving into the transition state. The plot of ln k *vs.* P (Fig. 1) is typical of a reaction with a positive volume of activation, which is 89 cm³ mol⁻¹ in this work
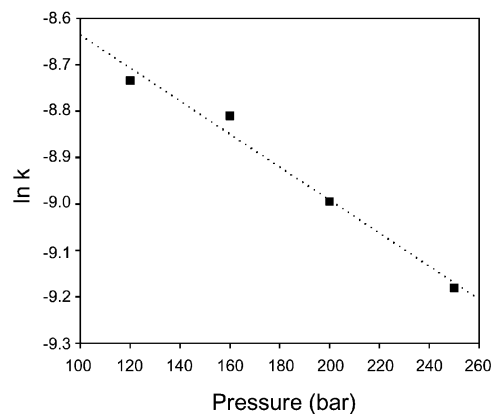

Fig. 1 Pressure dependence of the apparent rate constant for ROP of CL in sc CO₂ at 40 °C.

Table 1 Polymerisation of CL initiated by Bu₂Sn(OCH₃)₂ in supercritical carbon dioxide at various temperatures and pressures. (Time of reaction is 60 min, $[CL]_0 = 1.35$ M, $[CL]_0/[Sn]_0 = 131$, envisioned molecular weight is 15,000 g mol⁻¹)

Entry	Temperature (°C)	Pressure (bar)	Conversion (%)	Mn,calc × 10⁻³ (g mol⁻¹)ᵃ	Mn,SEC × 10⁻³ (g mol⁻¹)ᵇ	k (s⁻¹) × 10⁴
1	40	50	83	12.5	13.6 (1.4)	4.922
2	40	120	44	6.6	6.9 (1.2)	1.610
3	40	160	41	6.2	6.6 (1.2)	1.490
4	40	200	36	5.4	5.9 (1.2)	1.240
5	40	250	31	4.7	4.6 (1.2)	1.030
6	30	200	12	1.8	1.9 (1.1)	0.355
7	40	200	36	5.4	5.9 (1.2)	1.240
8	50	200	78	11.7	12.4 (1.5)	4.205
9	60	200	95	14.3	14.3 (1.6)	8.320

ᵃ Mn,calc = ([CL]₀/2 [Sn]₀) . M_CL . (conv./100). ᵇ Values obtained following size exclusion chromatography calibrated with polystyrene standards and using the *ad hoc* viscosimetric relationship. The values in between brackets stand for the polydispersity index (Mw/Mn) of the recovered samples.

compared to the −15 to −25 cm^3 mol^{-1} of many monomers in sc CO_2.[12] The high positive value of the volume of activation, together with the pressure-induced reduction in the rate of polymerisation, can be tentatively explained by Scheme 1, where Pn stands for a growing chain of *n* monomer units and Sn stands for the organotin species. This scheme is quite consistent with a high volume of activation, because CO_2 has to leave the chain for CL to be incorporated into the growing chain, so expanding the solvent shell and generating a transition state of a higher partial molar volume compared to the starting species. The effect of temperature was analyzed in a series of polymerisations conducted at various temperatures and a constant pressure of 200 bar. Data collected in Table 1 expectedly show the beneficial effect of increasing temperature upon the polymerisation kinetics. From these data and eqn. 2, the energy of activation can be calculated for the polymerisation, as shown in Fig. 2.[13]

$$\mathrm{d}\ln k/\mathrm{d}(1/T) = -E_a/R \quad (2)$$

The energy of activation (91 kJ mol^{-1}) is much higher than the value recorded when ROP of CL is conducted in toluene (65 kJ mol^{-1}). This observation is not surprising for a polymerisation reaction which is in competition with an inhibition reaction, *i.e.* the reversible conversion of the growing chains into dormant carbonate species. The higher energy of activation reflects that the extent of the inhibition reaction decreases with increasing temperature which is consistent with the endothermicity of the decarbonation reaction.

From the energy of activation and volume of activation, the free enthalpy of activation ($\Delta G^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) can be calculated by eqn. (3) and (4) derived from the Eyring's theory of the transition state.[13–14] These data are collected in Table 2 for polymerisation conducted in toluene and in sc CO_2, respectively.

$$E_a \cong \Delta H^{\neq} + RT - P\Delta V^{\neq} \quad (3)$$

$$\Delta S^{\neq}/4.576 = \log k - 10.573 - \log T + E_a/(4.576 \times T) \quad (4)$$
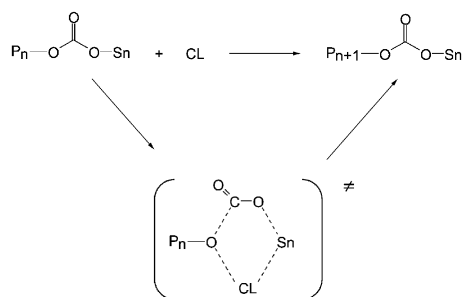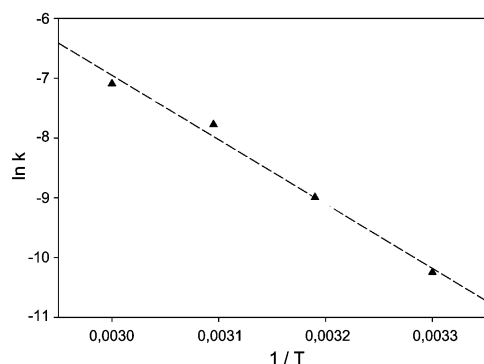

Scheme 1

Fig. 2 Arrhenius plot for the ROP of CL in precipitation in sc CO_2 at 200 bar and various temperatures.

Table 2 Parameters of activation for the polymerisation of CL initiated by $Bu_2Sn(OCH_3)_2$ in supercritical carbon dioxide. Envisioned molecular weight is 15,000 g mol^{-1} ([CL]$_0$ = 1.35 M, [CL]$_0$/[Sn]$_0$ = 131)

Temperature (°C)	$\Delta H^{\neq}$ (kJ mol^{-1}) [a]	$\Delta S^{\neq}$ (J $(mol.K)^{-1}$)[a]	$\Delta G^{\neq}$ (kJ mol^{-1})[a]
30	90.2	−32.7	100.1
40	90.2	−32.1	100.2
50	90.1	−31.4	100.2
60	90.0	−34.6	101.5
40[b]	62.9[b]	−64.9[b]	83.3[b]

[a] Polymerisation conducted in compressed carbon dioxide. [b] Polymerisation conducted in toluene at atmospheric pressure.

The free enthalpy of activation in sc CO_2 is higher by *ca.* 50% than the value noted in toluene. Importantly, the entropy of activation has similarly increased upon substitution of sc CO_2 for toluene. So, the negative entropy of activation typical of a coordination–insertion polymerization mechanism, is partly compensated by the expansion of the solvent shell (positive entropic contribution). That tin alkoxide responsible for the growth of the PCL chains is carbonated by compressed CO_2 has been confirmed by the infrared analysis of the initiator, *i.e.* dibutyltin dimethoxide, dissolved in sc CO_2 (10 w/v% of dibutyltin dimethoxide, 4 h at 40 °C and 200 bar) and later sprayed onto a NaCl disk. The spectrum of the sample shows a prominent peak at 1668 cm^{-1} typical of the carbonyl group of the carbonated initiator. Two additional intense peaks are observed at 1303 cm^{-1} and 1444 cm^{-1}, assigned to the symmetric and the antisymmetric stretchings of the O–C–O bonds of the carbonato group.

As a conclusion, this communication is additional strong evidence that tin alkoxide, that propagates the ε-CL polymerisation, is carbonated in sc CO_2 resulting in depressed polymerisation kinetics.

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