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Cationic and anionic ring-opening polymerization in supercritical CO_2

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SUMMARY: The ionic ring-opening polymerization of several heterocycles in supercritical CO_2 is described for the first time. Octamethylcyclosiloxane (D_4) as well as phenyloxazoline have been polymerized with cationic initiators (triflic acid or methyl triflate). The anionic and pseudo-anionic polymerizations of ε-caprolactone initiated respectively by t-BuOK and aluminum, yttrium or lanthanum isopropoxides are also reported. They are the first examples of anionic polymerization in the presence of CO_2 for which no incorporation of CO_2 has been observed in the resulting polymer, as evidenced by ^{13}C and ^{31}P NMR studies.

Introduction

During the last ten years, there has been an increasing interest in reducing the use of VOCs (volatile organic compounds) for environmental concern. In this context, supercritical CO_2 is an adequate reaction medium since it has a low toxicity, is inexpensive and non-flammable. Furthermore, it has easily accessible critical temperature and pressure and can be readily recycled[1)].

Most studies reported so far on polymerizations in supercritical fluids describe radical polymerization of vinyl monomers[1-3)]. In the case of ring-opening polymerization, only few examples are known: the cationic polymerization of oxetanes[4,5)], the ring-opening metathesis polymerization of norbornene and cyclooctene[6,7)] and the cationic polymerization of octamethylcyclotetrasiloxane[8)].

We report here results[9)] obtained in supercritical CO_2 on the anionic and pseudoanionic polymerization of ε-caprolactone (ε-CL), together with some obtained on the

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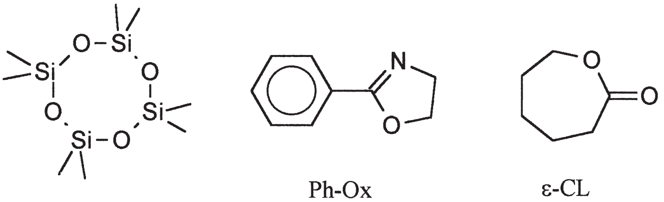
cationic polymerization of octamethylcyclotetrasiloxane (D_4) and phenyloxazoline (PhOx) (figure 1).



D_4 Ph-Ox ε-CL

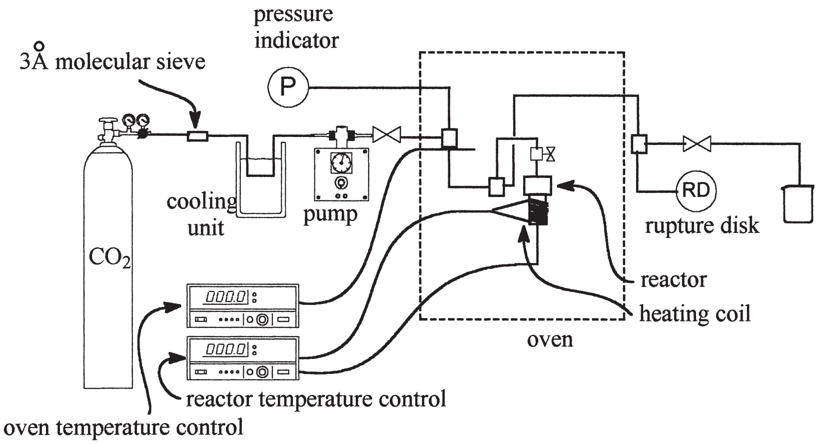
Figure 1. Structure of the monomers

Experimental part

Materials: ε-caprolactone, phenyloxazoline, and D_4 (Rhône-Poulenc) were dried over CaH_2 and trap-to-trap distilled under vacuum. CO_2 (Air Liquide) was dried over 3Å molecular sieves.

Polymerizations in supercritical CO_2: The experimental setup for supercritical polymerizations is represented in scheme 1. A 20ml reactor made of stainless steel was charged in a glove box with the monomer and a sealed glass ampoule containing the initiator. The reactor was then connected to the CO_2 line. Once the system has been purged and the pressure lowered to 1 bar, the connecting valve of the reactor was opened and the temperature raised to the desired one for the polymerization. A heating coil provided a slightly increased temperature at the base of the reactor leading to thermal agitation. When the system had reached equilibrium, CO_2 was pumped into the reactor. The ampoule was thus broken by CO_2 pressure between 60 and 130 bar, and this started the polymerization process.

When the reaction time was attained, the connecting valve was closed and the system depressurized. The reactor which was still under pressure was cooled down rapidly under running water and opened to evacuate CO_2. A solution of deactivating agent was then introduced in the reactor and the resulting polymer/monomer mixture analyzed by nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC).



Scheme 1. Experimental setup

Results and discussion

General considerations on polymerizations in supercritical fluids

When a polymerization is conducted in a supercritical fluid, several parameters may have an influence on the process: first the temperature and the pressure of the system which generate the supercritical conditions and secondly the physical properties of the supercritical fluid itself. The influence of the first parameters can be examined from two angles: kinetics or thermodynamics. They are summarized in table 1.

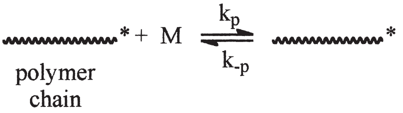
Table 1. Effect of temperature and pressure on a polymerization

	Temperature	Pressure
Kinetics	$k = Ae^{-\frac{E_a}{RT}}$	$\left.\frac{\partial \mathrm{Log}k}{\partial P}\right\|_T = -\frac{\Delta V^{\neq}}{RT} - K_T$
Thermodynamics	$\mathrm{Log}[M]_e = \frac{\Delta H_p}{RT_c} - \frac{\Delta S_p}{R}$	$\left.\frac{\partial \mathrm{Log}[M]_e}{\partial P}\right\|_T = \frac{\Delta V_p}{RT} + 2K_T$ $\frac{d\mathrm{Log}T_c}{dP} = \frac{\Delta V_p}{\Delta H_p}$

The effect of temperature on a polymerization is well-known. The rate constant is governed by Arrhenius' law, whereas depending on the sign of ΔH_p and ΔS_p, a ceiling temperature can be observed together with an equilibrium monomer concentration.

As for the effect of pressure, the variation of a rate constant can be related to the theory of activated complex[10,11]. This leads to the equation in table 1, where $\Delta V^{\neq}$ is the activation volume of the reaction and K_T corresponds to the compressibility of the system. In usual solutions, K_T is negligible. Thus, an increase in pressure will accelerate the chemical reaction if $\Delta V^{\neq}$ is negative, which is often the case for polymerizations. However, this effect becomes noticeable only for very high pressures, ca. 1000atm. For common experiments in supercritical fluids, the pressure used is rarely this high. Therefore, the influence of pressure will be often negligible. However, an increase in rate constants is observed near the critical point, due to the fluid steady change from a gaseous behaviour to a liquid-like one. Moreover, considerable discrepancies have been observed for the values of $\Delta V^{\neq}$ in this region, due to density fluctuations.

Using the same concept for polymerization/depolymerization equilibrium (1) leads to a variation of the monomer equilibrium concentration depicted in table 1. Logically, an increase in pressure will decrease $[M]_e$ if the variation of volume due to the polymerization is negative, which is often the case. As for ceiling temperature, its variation with pressure can be described by a Clausius-Clapeyron equation. Since, ΔV_p and ΔH_p are usually negative, this means that increasing the pressure will also increase the value of T_c.



(1)

In the particular case of D_4, ΔH_p is negligible and this ring is polymerizable because of a positive variation of entropy. This means that the temperature has no effect on the equilibrium between cycles and polymer. Pressure will then be the only efficient parameter for this system.

These effects of pressure and temperature are correct for any kind of fluid. In the case of supercritical fluids, their particular physical properties will also influence the polymerization process. The most attractive advantages are expected to be:

- decrease in system viscosity compared to classical polymerizations
- increase in diffusivity of the species
- tunable solvent/solute properties, enabling selective precipitation

- easy purification of polymer.

In order to characterize more thoroughly the effect of supercritical medium on ring-opening polymerization, we have chosen three types of rings and studied their polymerization in supercritical CO_2.

In all cases, identical reactions were carried out in toluene at the same temperature but under atmospheric pressure. In the case of cyclosiloxanes, polymerizations were compared both at same monomer mass percentage and at same monomer mole fraction. As for other monomers, they were compared at same monomer mass percentage. Polymer formation was characterized by the percentage of polymer in the final product.

Polymerization of cyclosiloxanes and phenyloxazoline

The results obtained for D_4 are presented in table 2. As reported in Rhône-Poulenc patent[8)], the cationic polymerization of D_4 initiated with triflic acid (TfOH) can lead to a polydimethylsiloxane with low polydispersity. In this case, comparing the experiments at same mole fraction shows a great influence of the pressure, since the percentage of polymer obtained varies from 18% at 1bar to 80% at 200bar.

Table 2. Polymerization of D_4 in supercritical CO_2.

Initiator	Solvent	[M]/[I]	%M[a]	x[b]	P_a[c] (bar)	T (°C)	P[d] (bar)	t[e] (min)	%Pol.[f]	$\overline{M_n}_{exp}$[g]	I[h]
TfOH	CO_2	36	0.48	0.12	130	125	150	15	56	168000	1.5
		35	0.48	0.12	40	110	150	60	77	77800	5.8
		35	0.41	0.09	120	110	200	60	80	121000	2.3
	Toluene	35	0.48	0.22		110	1	15	64	14800	3.4
		35	0.27	0.1		110	1	60	18	4500	1.8
TfOMe	CO_2	30	0.48	0.12	68	113	150	360	40	134000	1.9
			0.48	0.12	110	110	150	360[i]	-	-	
	Toluene	30	0.48	0.22		110	1	1080	-		

a: monomer mass percentage. b: monomer mole fraction. c: pressure for which the ampoule breaks. d: pressure in the reactor. e: time of polymerization. f: polymer yield. g: experimental $\overline{M_n}$ of crude polymer determined by SEC. h: $\overline{M_w}/\overline{M_n}$. i: realized in the presence of a proton trap.

A slow polymerization was observed in the presence of methyl triflate leading to 40% of polymer in 6h. However, when the same experiment was repeated in the presence of a proton trap, ditert-butyl 4-methyl pyridine, no polymer was obtained. This means that the polymerization was in fact initiated by methyl triflate together with traces of triflic acid, which is probably formed from residual traces of water in CO_2. The same has already been described in regular solutions[12]).

As for the case of Ph-Ox (table 3), although the system is presumably biphasic, a total conversion of monomer is obtained and the molecular weight distribution is relatively narrow; this indicates that organic solvents are not mandatory for this kind of polymerization. The system is very comparable to the solution polymerization in toluene. Indeed, if this system is monophasic at the beginning, it becomes quickly biphasic as the polymer begins to form. This leads to a very narrow distributed polymer in excellent yields. The reaction proceeds exactly the same way in supercritical CO_2 and the yields and molar masses are quite similar. Only the polydispersity index seems to be slightly larger in CO_2. By increasing the [M]/[I] ratio, an increase in molecular weight is observed and the polydispersity index becomes slightly larger. In this case, the end groups are not detected by ^1H NMR. The value of $\overline{M_n}$ has been calculated from SEC chromatogram and a correcting factor previously determined for oligomers.

Table 3. Polymerization of PhOx initiated by TfOMe.

Solvent	[M]/[I]	%M^a	$P_a{}^b$ (bar)	T (°C)	P^c (bar)	t^d (min)	%Pol.	$\overline{M_n}_{exp}$	I	$\overline{M_n}_{th}$
CO_2	43	0.45	25	(230)	151	350	85	7900	1.15	6450
	43	0.45	80	115	200	350	>90	5000	bimodal distribution	6450
	43	0.26	80	115	150	360	>90	4700	1.5	6450
	154	0.26	160	110	150	360	98	13800^e	1.7	22600
Toluene	43	0.26		110	1	300	97	9100	1.1	6450
Acetonitrile	50	0.26		81	1	360	85	8800	1.4	7400

a: monomer mass percentage. b: pressure for which the ampoule breaks. c: pressure in the reactor. d: time of polymerization. e: calculated from $\overline{M_n}_{SEC} \times 2.5$

Polymerization of ε-caprolactone

The anionic polymerization of ε-caprolactone has been studied for a long time and is a well-known process[13]). Its main characteristic is the existence of secondary reactions, such as reshuffling and back-biting (inter- and intramolecular reactions). This leads to quite large molecular weight distributions. In 1975, Teyssié and coll. developed aluminum alkoxide initiators which lead to narrow distributions and no side-reactions, at least simultaneously to polymerization[14]). In 1992, Mc Lain and coll. proposed the use of yttrium or lanthanide alkoxides in order to obtain a very fast conversion and suppress the side-reactions at ambient temperature[15)].

The polymerizations were thus carried out using these initiators either in toluene or in bulk at atmospheric pressure and 110°C, which is the temperature of the supercritical reaction. At this temperature, it is clear that the side-reactions are more favored than at ambient temperature, since the polydispersity indexes range between 1.5 and 2.0 versus typically 1.2 at ambient temperature[15)] (table 4). Nevertheless, with lanthanide initiators, the polymer distribution does not change after the completion of polymerization (typically completed within one minute) and at least up to 15min, which is the time of reaction that we chose for the supercritical systems. At ambient temperature, it has been shown that the average number f of growing chain per metal atom is close to 1 in the case of ε-caprolactone. The experimental value at 110°C is comparable.

Table 4. Polymerization of ε-caprolactone in solution at 110°C.

Initiator	Solvent	%M^a	[M]/[I]	t^b (min)	%Pol.	$\overline{M_n}_{exp}$	I	$\overline{M_n}_{th}$	f^c
tBuOK	Toluene	0.13	49	15	35(65 of cycles)	17500	2.0	5700	
$Al(OiPr)_3$	Toluene	0.13	45	180		2600	2.4	1700	
	-	1	45	15	90	5100	3.1	1700	
$Y(OiPr)_3$	Toluene	0.13	47	15	95	4380	1.6	1800	1.2
	Toluene	0.13	146	15		7800	1.8	5550	
	-	1	47	15		5180	8.0	1800	
$La(OiPr)_3$	-	1	32	15		7300	6.2	1200	
	Toluene	0.13	140	3	80	14600	1.5	5300	0.9
	Toluene	0.13	140	7	80	16500	1.5	5300	
	Toluene	0.13	140	15	70	10800	1.7	5300	

a: monomer mass percentage. b: time of polymerization. c: calculated from f=3.%Pol. $\overline{M_n}_{th}/\overline{M_n}_{exp}$

In bulk, since the initiator is not very soluble in the monomer, the system is heterogeneous right from the beginning of the reaction and this leads to very large distributions.

The same reactions were then performed in supercritical CO_2. The results are presented in table 5. It is somewhat surprising that polymers can be obtained in these conditions, since an alkoxide group should react with CO_2 yielding a carbonate group which is unable to initiate the polymerization of ε-caprolactone. Therefore, it can be supposed that, under our experimental conditions, the propagation occurs faster than this side-reaction with

CO_2. Since the values of the polydispersity indexes are very different from those obtained in bulk and are closer to those measured for solution experiments, we can assume that the system behaves as a diluted phase in supercritical CO_2, and that the polymerization does not take place in a totally CO_2-separated phase. However, it is not possible to exclude at this stage of the experiments the possibility of CO_2-swelled bulk droplets suspended in supercritical CO_2 phase.

Table 5. Polymerization of ε-caprolactone in supercritical CO_2[a].

Initiator	[M]/[I]	P_a[b] (bar)	T (°C)	P^c (bar)	t^d (min)	%Pol.	$\overline{Mn}_{exp}$	I	$\overline{Mn}_{th}$	f^e
tBuOK	49	120	108	155	15	7	6000	2.0	5600	
Al(OiPr)$_3$	45	30	110	150	180	80	10400	2.9	1700	0.4
	51	130	110	150	120	95	8300/ 260000	1.6/ 2.8	1950	
	51	200	110	190	15	82	7650	2.3	1950	0.6
Y(OiPr)$_3$	47	128	112	153	15	90	1970	2.1	1800	2.5
	58	75	106	150	15	95	15400	1.8	2220	0.4
	137	40	110	150	15	85	5500	2.5	5550	2.6
	155	60	110	150	15	70	10300	1.8	5900	1.2
La(OiPr)$_3$	140	30	110	150	15	25	5050	1.4	5250	

a: monomer mass percentage %M=0.13. b: pressure for which the ampoule breaks. c: pressure in the reactor. d: time of polymerization. e: calculated from $f=3.\%Pol.\ \overline{Mn}_{th}/\overline{Mn}_{exp}$

However, two types of behaviour are clearly observed depending on the initiator. For tBuOK and La(OiPr)$_3$, the yield of polymer is always low. This indicates some reactions between the anionic species and CO_2. On the other hand, for initiators like Al(OiPr)$_3$ or Y(OiPr)$_3$, the yield in polymer is comparable to that in bulk or solution polymerization.

In the case of aluminum isopropoxide, the experimental molar mass is higher than the theoretical one, probably because of a low solubility of the initiator, which decreases its efficiency. In one experiment, even a bimodal distribution was obtained in SEC with a population of very high molecular weight, which accounted for 50% in mass. Although this result is right now not well understood, it could arise from the presence of a separated phase in the polymerization medium. A comparable behaviour is observed at 200 bar: the efficiency of the initiator is still poor and the SEC chromatogram shows a shoulder on the polymer peak.

As for yttrium isopropoxide, the value of $\overline{Mn}_{exp}$ does not show a clear dependence on [M]/[I] ratio. The fluctuation of the molar mass can be interpreted as differences in initiator efficiency between experiments, as shown by the variation of the average number of growing chain per metal atom f. Although temperature and pressure are easily controlled, the breaking of the ampoule is indeed uncontrolled. It is then possible that the initiator in part remains in the broken ampoule and is not used for the initiation reaction. In the near future, the set-up will be changed in order to better control the introduction of the initiator.

The difference between tBuOK, La(OiPr)$_3$ and the other initiators could stem from different ionic characters. As a matter of fact, it is well known that the polymerization of ε-CL initiated by aluminum alkoxides is a pseudoanionic process and the active centers are in fact more covalent than ionic14,16). As for Y(OiPr)$_3$, the problem of the polymerization mechanism has not been solved yet. If the active centers are less ionized, they do not react so quickly with CO_2. Indeed, the IR spectra of polymers synthesized with these initiators in the presence of CO_2 show only one carbonyl band at 1726cm^{-1} and are exactly the same as a sample prepared in solution, corroborating the fact that CO_2 does not react during the polymerization. This result has been confirmed by ^{13}C NMR spectra which show only one carbonyl peak at 174.3ppm corresponding to the regular position for poly(ε-CL). This shows that there is no regular incorporation of CO_2 in the polymer chain.

In order to examine possible reactions between active species and carbon dioxide after completion of the polymerization, some experiments were deactivated with a phosphorus reagent according to a method proposed by Penczek17). In the presence of alkoxides, the reaction with diphenylchlorophosphate leads to a phosphate with a ^{31}P NMR signal around –10ppm, whereas by reaction onto carboxylate ions a phosphorylated anhydride is obtained with a ^{31}P NMR signal at –25 ppm. Parallel polymerizations were thus realized in toluene or supercritical CO_2 and deactivated with this reagent. The results are presented in table 6 and reveal that both polymers present the same ^{31}P NMR spectrum and no signal was observed at –25ppm. Therefore, no incorporation of CO_2 has taken place in the supercritical experiment, even after completion of the polymerization. However, two signals were observed in each case, corresponding to two types of alkoxydes. The reason of this is still unclear at this time.

Table 6. ^{31}P NMR characterization of active species

Initiator	Solvent	$\overline{M_n}_{exp}$	I	^{31}P NMR
Y(OiPr)$_3$	Toluene	5100	2.0	-11.6/-10.6
	CO_2	6100	1.8	-11.6/-10.6
Al(OiPr)$_3$	Toluene	29000	1.5	-11.7/-10.7
	CO_2	9450	2.0	-11.7/-10.7

Contrary to ε-CL, cyclosiloxanes do not polymerize anionically in supercritical CO_2. This difference of behavior indicates that anionic polymerization can be realized in CO_2 if the initiator and the active species are well chosen and are not too ionic, in order not to react with CO_2.

Conclusion

The ring-opening polymerization of various cycles has thus been realized in the presence of supercritical CO_2. The cationic polymerization of cyclosiloxane D_4 and phenyloxazoline has been observed. Further studies on the influence of pressure and temperature are in progress. In the case of ε-caprolactone, the results in anionic polymerization will be investigated in detail. More specifically, for these three monomers, a thorough study will have first to determine the phase diagrams of the system monomer/polymer/CO_2 using a reactor with a sapphire window, in order to examine the homogeneity of the solutions.

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