Cationic and Anionic Ring-Opening Polymerization in Supercritical CO_2. Preliminary Results

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ABSTRACT: 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). Anionic and pseudo-anionic polymerizations of ε-caprolactone initiated respectively with tBuOK and isopropoxides of aluminum, yttrium and lanthanum 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.
    KEY WORDS   Ring-Opening Polymerization / Supercritical Fluid / Supercritical Carbon Dioxide / Siloxanes / Oxazolines / Lactones /

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

Most studies so far on polymerizations in supercritical fluids describe radical polymerization of vinyl monomers.[1-3] In the case of ring-opening polymerization, only a 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]

Among published studies, only one describes anionic polymerization of styrene in supercritical butane,[9] and few deal with anionic polymerization of oxiranes leading to poly(ethers-co-carbonates) by incorporation of CO_2 in the polymer.[10-14] This year, Holmes et al. reported the polymerization of monosubstituted epoxides in supercritical CO_2 with rare earth catalysts; the reactions under these conditions lead exclusively to polyethers in low yields.[15]

We report here preliminary results obtained in supercritical CO_2 on the anionic and pseudo-anionic polymerization of ε-caprolactone (ε-CL), together with some on the cationic polymerization of octamethylcyclotetrasiloxane (D_4) and phenyloxazoline (PhOx) (Figure 1). By polymerization, these monomers lead to respectively polyesters, polysiloxanes and polyamides which represent three leading categories of polymers. They are all of particular interest because of their mechanical properties and biological applications in the case of polyesters, because of wide applications in surface protection for silicones, and potential use as amphiphiles for poly(oxazolines). Moreover, the cationic polymerization of oxazolines being a living process, this constitutes a simple system to study the influence of pressure on polymerization.

EXPERIMENTAL

Materials

ε-CL, phenyloxazoline, D_3 (Aldrich) and D_4 (Rhône-Poulenc) were dried over CaH_2 and trap-to-trap distilled under vacuum. CO_2 (Air Liquide) was dried over 3 Å molecular sieves. Acetonitrile was dried over CaH_2 and trap-to-trap distilled. Toluene was distilled over CaH_2, stocked over sodium mirror and trap-to-trap distilled.

### Polymerizations in Supercritical CO_2

The experimental setup for supercritical polymerizations is represented in Scheme 1. A 20 ml reactor made of stainless steel was charged in a glove box with monomer and a sealed glass ampule containing the initiator. The reactor was connected to the CO_2 line. Once the system had been purged and 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 bottom of the reactor leading to thermic agitation. When the system had reached equilibrium, CO_2 was pumped into the reactor. The ampule was thus broken by CO_2 pressure between 60 and 130 bar, and this started the polymerization.

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

Polymerizations in Regular Solvents

The experiments were carried out under nitrogen in flame-dried three-necked flasks. The monomer and solvent were introduced into the flask under nitrogen. The solution was heated to the desired temperature

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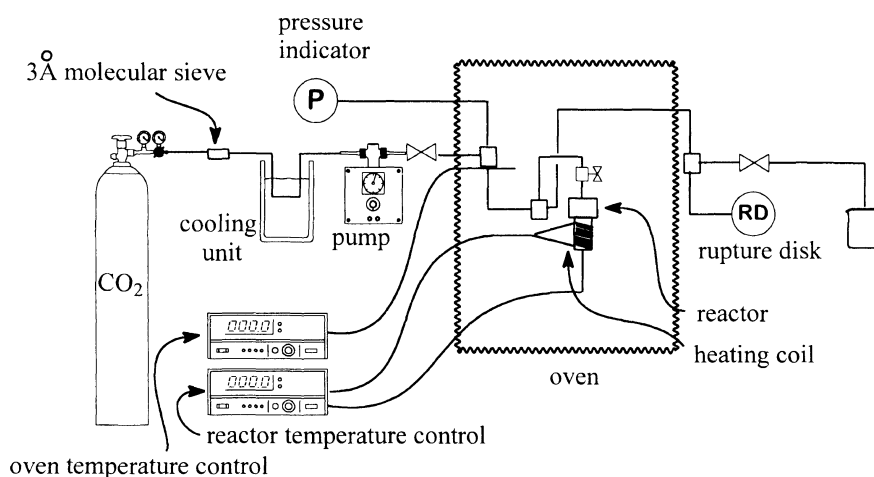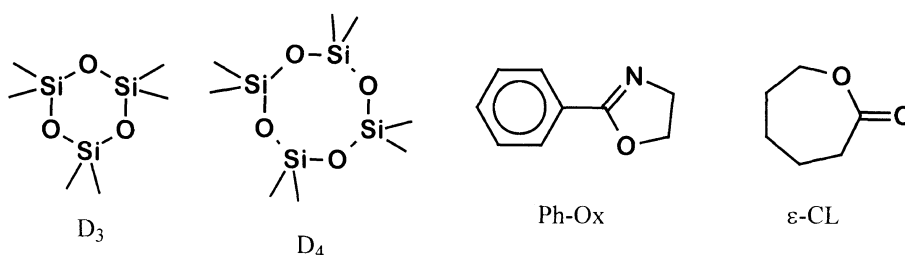
Scheme 1. Experimental setup.

Figure 1. Structure of the monomers.

and initiator was added.

Characterizations

^{1}H NMR spectra were recorded on a Bruker AC200 at 200 MHz in $CDCl_3$. Number-average molecular weights of the polymers ($\bar{M}_n$) were determined by NMR for polyphenyloxazoline or by SEC for other polymers, in tetrahydrofuran (THF) or in toluene, on a Varian apparatus equipped with a TSK column pack (HXGL 4000, HXGL 3000, HXGL 2000) and refractive index detection. Average molecular weights were calculated using a polystyrene calibration curve. The validity of this calibration curve (within the experimental error) was checked by light scattering detection experiments (Wyatt Dawn SSP) coupled with SEC. Polymer yield was quantified either by NMR, SEC, or by gravimetry after precipitation.

RESULTS AND DISCUSSION

In all cases, to show the influence of supercritical medium on polymer formation, identical reactions were carried out in toluene at the same temperature but under atmospheric pressure. In preliminary experiments, we found that the closest results between supercritical fluid and regular solution polymerizations were obtained for the same monomer mass percentage, and not for identical monomer concentration (in $mol\,l^{-1}$) or mole fraction x. Therefore, in all experiments, the results were compared for similar 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_3 (Figure 1) and D_4 are presented in Tables I and II. Firstly, anionic polymerization does not occur, either with D_4 or D_3, contrary to the case of ε-CL as will be further discussed.

As reported in Rhône-Poulenc patent[8], the cationic polymerization of D_4 initiated with triflic acid (TfOH) leads to polydimethylsiloxane with low polydispersity. Under these conditions, methyl triflate (TfOMe) can initiate the polymerization, which is not possible under usual conditions. However, it is necessary to verify in further experiments whether the initiator reacts directly or whether its reaction is catalyzed by TfOH traces (possibly from the hydrolysis of TfOMe by traces of water in CO_2).

The polymerization initiated by methyl triflate is very slow compared to that with triflic acid. The influence of reaction time indicates an increase in polymer yield between 2.5 h and 6 h from 23% to 40%. This means that the equilibrium between polymer and cyclics is not yet reached within 6 h. Some experiments were realized at different pressures or temperatures. In our case, increasing the pressure to 200 bar or the temperature to 130°C lowered the yield and the molar mass. This is contrary to what Lebrun and coll. reported.[8] In their case, increasing the pressure lowered the yield and molar mass of the polysiloxanes, but an increase of temperature had the reverse effect. However, since the polymerization conditions are quite different here, and the initiator not the same, a comparison of both systems might not be straightforward. Further experiments using wider range of pressure and temperature should be made to characterize their influence.

As for Ph-Ox (Tables III and IV), although the system

Table I. Polymerization of cyclosiloxanes in supercritical CO_2[a]

M	Initiator	P_a[f] (bar)	T_{int}[g] (°C)	T_{ext}[h] (°C)	P[i] (bar)	t[k] (min)	%Pol.[l]	$\bar{M}_{n\,exp}$[m]	I[n]	$\bar{M}_{n\,th}$[o]
D_4	Me₃SiOK[b]	20		110	150	240		—		
	PDMSSiOK[b]	25		110	153	240	6	3200	1.4	14800
D_3	tBuOK[c]	58	110	98	100	5	—			
D_4	TfOH[d]	130	125	105	150	15	56	168000	1.5	10700
	TfOMe[e]	50	100	110	150	150	23	15900	3.5	8900
		68	113	97	150	360	40	134000	1.95	8900
		60	118	110	200[j]	150	16	11400	4.7	8900
		56	140	130	150	150	9	6600	5.5	8900

[a] Monomer mass percentage %M = 0.48. [b] [M]/[I] = 50, PDMSSiOK: potassium silanolate oligomers. [c] [M]/[I] = 100. [d] [M]/[I] = 36. [e] [M]/[I] = 30. [f] Pressure for which the ampule breaks. [g] Internal reactor temperature. [h] Oven temperature. [i] Pressure in the reactor. [j] %M = 0.41. [k] Time of polymerization. [l] Polymer yield. [m] Experimental $\bar{M}_n$ of crude polymer determined by SEC. [n] $\bar{M}_w/\bar{M}_n$. [o] Theoretical $\bar{M}_n$ of polymer determined from [M]/[I] and molar mass of monomer.

Table II. Polymerization of cyclosiloxanes in toluene[a]

Monomer	Initiator	[M]/[I]	t[b] min	%Pol.[c]	$\bar{M}_{n\,exp}$[d]	I[e]	$\bar{M}_{n\,th}$
D_4	Me₃SiOK	50	1080	64	8900	1.8	14800
D_3	tBuOK	50	5	58	39900	2.0	11100
D_4	TfOH	35	15	64	14800	3.4	10400
	TfOMe	30	1080	—			

[a] T = 110°C, P = 1 bar and %M = 0.48. [b] Time of polymerization. [c] Polymer yield. [d] Experimental $\bar{M}_n$ of crude polymer determined by SEC. [e] $\bar{M}_w/\bar{M}_n$.

Table III. Polymerization of PhOx in supercritical CO_2 initiated by TfOMe[a]

%M[b]	P_a[c] (bar)	T_{int}[d] (°C)	T_{ext}[e] (°C)	P[f] (bar)	t[g] (min)	%Pol.[h]	$\bar{M}_{n\,exp}$[i]	I[j]	$\bar{M}_{n\,th}$
0.45	25	(230)	110	151	350	85	7900	1.15	6350
0.45	80	115	110	200	350	>90	5000	Bimodal distribution	6350
0.26	80	115	110	150	360	>90	4700	1.5	6350

[a] [M]/[I] = 43. [b] Monomer mass percentage. [c] Pressure for which the ampule breaks. [d] Internal reactor temperature. [e] Oven temperature. [f] Pressure in the reactor. [g] Time of polymerization. [h] Polymer yield. [i] Experimental $\bar{M}_n$ of crude polymer determined by NMR. [j] $\bar{M}_w/\bar{M}_n$.

Table IV. Polymerization of PhOx initiated by TfOMe in solution[a]

Solvent	[M]/[I]	T/°C	t[b]/min	%Pol.[c]	$\bar{M}_{n\,exp}$[d]	I[e]	$\bar{M}_{n\,th}$
Toluene	43	110	300	97	9100	1.1	6450
Acetonitrile	50	81	360	85	8800	1.4	7400
—	50	110	35	77	8150	1.2	7400

[a] P = 1 bar and %M = 0.26. [b] Time of polymerization. [c] Polymer yield. [d] Experimental $\bar{M}_n$ of crude polymer determined by NMR. [e] $\bar{M}_w/\bar{M}_n$.

is presumably biphasic, 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 quite comparable to 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 narrowly distributed polymer in excellent yields. The reaction proceeds exactly the same way in supercritical CO_2 and yields and molar masses are quite similar. Only the polydispersity index seems slightly larger in CO_2.

Polymerization of ε-Caprolactone

The anionic polymerization of ε-CL has been studied for a long time and is a well-known process.[16] 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. This is typically the case with tBuOK used as initiator, in solution or in bulk conditions (Table V). In 1975, Teyssié et al. developed aluminum alkoxide initiators which lead to narrow distributions and no side-reactions, at least simultaneously to polymerization.[17] In 1992, McLain et al. proposed the use of yttrium or lanthanide alkoxides to obtain very fast conversion and suppress side-reactions at ambient temperature.[18]

Polymerizations were thus carried out using these initiators either in toluene or in bulk at atmospheric pressure and 110°C, the temperature of the supercritical

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

Initiator	Solvent	%M^a	[M]/[I]	t^b/min	%Pol.^{c}	$\bar{M}_{n\,exp}{}^d$	I^e	$\bar{M}_{n\,th}{}^f$	f^g
tBuOK	Toluene	0.13	49	15	35 (65 of cycles)	17500	2.0	5700	
—		1	49	15		2540	7.6	5700	
Al(OiPr)$_3$	Toluene	0.13	45	180		2600	2.4	1700	1.5^h
		1	45	15	90	5100	3.1	1700	
Y(OiPr)$_3$	Toluene	0.13	47	15	95	4380	1.6	1800	1.1^i
	Toluene	0.13	146	15		7800	1.8	5550	2.1^h
—		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^i
	Toluene	0.13	140	7	80	16500	1.5	5300	0.8^i
	Toluene	0.13	140	15	70	10800	1.7	5300	1.0^i

^{a} Monomer mass percentage. ^{b} Time of polymerization. ^{c} Polymer yield. ^{d} Experimental $\bar{M}_n$ of crude polymer determined by SEC or NMR. ^{e} $\bar{M}_w/\bar{M}_n$. ^{f} Theoretical $\bar{M}_n$ of polymer calculated from [M]/[I] for tBuOK and [M]/3[Mt(OR)$_3$] for the other initiators. ^{g} Average number of growing chains per metal atom. ^{h} Calculated from 3. $\bar{M}_{n\,th}/\bar{M}_{n\,exp}$. ^{i} Calculated from 3.%Pol. $\bar{M}_{n\,th}/\bar{M}_{n\,exp}$.

Table VI. Polymerization of ε-caprolactone in supercritical CO$_2{}^a$

Initiator	[M]/[I]	$P_a{}^b$ / bar	$T_{int}{}^c$ / °C	$T_{ext}{}^d$ / °C	P^c / bar	t^f / min	%Pol.^{g}	$\bar{M}_{n\,exp}{}^h$	I^i	$\bar{M}_{n\,th}{}^j$	f^k
tBuOK	49	120	108	97	155	15	7	6000	2.0	5600	
	116	80	110	100	150	15	5	6500	2.0	13200	
Al(OiPr)$_3$	45	30	110	100	150	180	80	10400	2.9	1700	
	51	130	110	100	150	120	95	8300/ 260000	1.6/ 2.8	1950	
Y(OiPr)$_3$	47	128	112	100	153	15	90	1970	2.1	1800	2.5^l
	58	75	106	100	150	15	95	15400	1.8	2220	0.4^l
	137	40	110	100	150	15	85	5500	2.5	5550	2.6^l
	155	60	110	100	150	15	70	10300	1.8	5900	1.2^l
La(OiPr)$_3$	140	30	110	100	150	15	25	5050	1.4	5250	0.8^l
	460	85	107	100	150	15	5	1600	2.6	17500	

^{a} Monomer mass percentage %M = 0.13. ^{b} Pressure for which the ampule breaks. ^{c} Internal reactor temperature. ^{d} Oven temperature. ^{e} Pressure in the reactor. ^{f} Time of polymerization. ^{g} Polymer yield. ^{h} Experimental $\bar{M}_n$ of crude polymer determined by SEC. ^{i} $\bar{M}_w/\bar{M}_n$. ^{j} Theoretical $\bar{M}_n$ of polymer calculated from [M]/[I] for tBuOK and [M]/3[Mt(OR)$_3$] for the other initiators. ^{k} Average number of growing chains per metal atom. ^{l} Calculated from 3.%Pol. $\bar{M}_{n\,th}/\bar{M}_{n\,exp}$.

reaction. At this temperature, it is clear that 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[18] (Table V). Nevertheless, with lanthanide initiators, the polymer distribution does not change after completion of polymerization (typically completed within one minute) and at least up to 15 min, which is the time of reaction that we chose for the supercritical systems.

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 distribution.

The number of growing chains per metal (Al, La···) in these systems has been shown to vary according to monomer, temperature and even [M]/[I] ratio.[19,20] At 110°C, in our conditions, the average number of initiating alkoxide groups was slightly higher than 1.

The same reactions were performed in supercritical CO$_2$. The results are presented in Table VI. 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, under our experimental conditions, propagation possibly occurs faster than this side-reaction with CO$_2$. Since 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 polymerization does not take place in a totally CO$_2$-separated phase. However, it is not possible to exclude at this stage the possibility of CO$_2$-swelled bulk droplets suspended in supercritical CO$_2$ phase.

However, two types of behavior are clearly observed depending on the initiator. For tBuOK and La(OiPr)$_3$, the yield of polymer is always lower than that in the corresponding bulk or solution polymerization. This indicates some reactions between the anionic species and CO$_2$. For initiators like Al(OiPr)$_3$ or Y(OiPr)$_3$, the yield of polymer is comparable to that in bulk or solution polymerization. This may mean that in these cases the active center is less ionized and thus does not react so quickly with CO$_2$. Indeed, the IR spectra of polymers synthesized with these initiators in the presence of CO$_2$ showed only one carbonyl band at 1726 cm^{-1} and were exactly the same as a sample prepared in solution, corroborating the fact that CO$_2$ does not react during the polymerization. This was confirmed by ^{13}C NMR spectra which show only one carbonyl peak at 174.3 ppm corresponding to the regular position for poly-(ε-CL). This shows that there is no regular incorporation of CO$_2$ in the polymer chain. The polymerization of ε-CL initiated by aluminum alkoxides is a pseudo-ani-

onic process and the active centers are more covalent than ionic.[15,21] As for Y(OiPr)₃, the problem of the polymerization mechanism has not been solved yet. Further experiments are in progress to determine the structure of the chain ends which will give more indication about reactions of the active centers after completion of polymerization.

In the case of aluminum isopropoxide, the experimental molar mass is higher than the theoretical one, probably because of low solubility of the initiator, which decreases its efficiency. In one experiment, even a bimodal distribution was obtained in SEC with a population at very high molecular weight, accounting for 50% in mass. Although this is not well understood, it could arise from the presence of a separated phase in the polymerization medium.

As for yttrium isopropoxide, $\bar{M}_{nexp}$ does not show a clear dependence on [M]/[I] ratio. The average number of growing chains per metal can be estimated between 0.4 and 2.6. Fluctuation of the molar mass can be interpreted as difference in initiator efficiency. Although temperature and pressure are easily controlled, the breaking of the ampule is indeed uncontrolled. It is thus possible that the initiator in part remains in the broken ampule and is not used for the initiation reaction. In the near future, the set-up will be changed to better control the introduction of the initiator.

The difference of behavior for ε-CL and cyclosiloxanes indicates that anionic polymerization can be realized in CO₂ if the initiator is well chosen and is not too ionic, in order not to react with CO₂.

CONCLUSION

The ring-opening polymerization of various cycles was realized in the presence of supercritical CO₂. The cationic polymerization of cyclosiloxane D₄ and phenyloxazoline was observed. Further studies on the influence of pressure and temperature are in progress. In the case of ε-CL, 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/CO₂ using a reactor with a sapphire window, to examine the system homogeneity.

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