Synthesis and Characterization of Random Copolyesters of ϵ-Caprolactone and 2-Oxepane-1,5-dione

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ABSTRACT: 2-Oxepane-1,5-dione (OPD) has been synthesized by the Baeyer−Villiger oxidation of 1,4-cyclohexanedione and copolymerized with ϵ-caprolactone. This random copolymerization has been initiated by different metal derivatives, i.e., tin octanoate, dibutyltin dimethoxide, and aluminum isopropoxide. Dibutyltin dimethoxide is the preferred initiator, and the course of polymerization is controlled by the competition of the ketone of OPD and the ester of the lactones for coordination to the initiator. Semicrystalline copolymers are formed, whose the randomness has been confirmed by DSC, ^{1}H NMR, and ^{13}C NMR analysis. A single melting temperature (T_m) has been observed, which varies regularly and monotonically with the OPD content as result of a cocrystallization phenomenom. The single glass transition temperature (T_g) obeys the Fox equation.

Introduction

Nowadays, the environmental concern is rapidly growing, which justifies the attention paid to biodegradable materials.[1] Aliphatic polyesters, such as poly-ϵ-caprolactone (PCL) and polylactides (PLA), are biomaterials with potential application in the medical and/or ecological fields. They can indeed contribute to the medical care of patients and to keep the earth environment clean and safe.

However, the applicability of these thermoplastics may be limited by the too low melting temperature of PCL (60 °C) and glass transition of the amorphous poly-DL-lactide (50 °C). There are several strategies useful to extend the range of the PCL and PLA properties, among which blending, copolymerization, chemical modification, and design of the macromolecular architecture may be cited. Copolymerization is the more general strategy for increasing the potential of the existing polymeric materials. Indeed, changing the structure, content, and distribution of the comonomers may lead to a variety of completely new materials, as is illustrated by the styrene and butadiene copolymerization, which may lead to random SBR rubber and to thermoplastic elastomers of the SBS triblock type.[2]

ϵ-Caprolactone (ϵ-CL) has been randomly copolymerized with numerous cyclic monomers until now, including β-butyrolactone, γ-valerolactone, lactides, glycolide, ϵ-caprolactam, ω-laurolactam, and 1,5-dioxepan-2-one.[3−8] More recently, ϵ-CL has been copolymerized with several substituted ϵ-caprolactones, such as γ-methyl-CL, γ-*tert*-butyl-CL, γ-ethylene ketal-CL (TOSUO), γ-(trialkylsilyloxy)-CL, γ-bromo-CL, and 7-allyl-1-oxa-cycloheptan-2-one.[9−14] All these copolymerization reactions modify properties such as crystallinity, melting temperature, thermal stability, biodegradability, etc. When the melting temperature of PCL is concerned, we have recently reported that it could be increased by random copolymerization of ϵ-caprolactone with 2-oxepane-1,5-dione (OPD),[15] which results from the substitution of a carbonyl for the methylene in the γ-position in the ϵ-CL cycle. This paper aims at reporting on a more detailed analysis of this copolymerization initiated by different metal derivatives, including tin octanoate [$Sn(Oct)_2$], aluminum isopropoxide [$Al(O^iPr)_3$], and dibutyl tin dimethoxide [$Bu_2Sn(OCH_3)_2$], that are commonly used as initiators for the ROP of lactones and lactides. Randomness of the copolymerization has been assessed by ^{13}C NMR spectroscopy, whereas the thermal transitions have been analyzed by DSC in relation to the copolymer composition.

Experimental Section

Materials. ϵ-Caprolactone (Aldrich), cyclohexanone (Aldrich), and 1-butanol (Aldrich) were dried over CaH_2 (Aldrich) for 48 h and distilled under reduced pressure, prior to use. 2-Oxepane-1,5-dione (OPD) was synthesized by the Baeyer−Villiger oxidation of 1,4-cyclohexanedione as reported elsewhere.[15] Tin bis(2-ethylhexanoate) (tin octanoate, Tegokat 129, from Goldschmidt AG) and dibutyltin dimethoxide (Aldrich) were used as received. Toluene was purified by refluxing over a benzophenone−Na complex and distilled under nitrogen prior to polymerization. Aluminum isopropoxide (Aldrich) was sublimated twice and dissolved in previously dried toluene.

(Co)polymerization of ϵ-CL and OPD. In a typical example, OPD (46.9 mmol) was weighed in a glovebox and placed in a previously flamed glass reactor, followed by the addition of dry toluene (10 mL). A homogeneous solution was formed at 90 °C and added with the initiator, e.g., a tin octanoate (0.47 mmol) solution in (5 mL) dry toluene. This solution was added through a rubber septum with a previously flamed syringe. Polymerization was conducted at 90 °C under stirring. Polymerization of ϵ-CL was carried out according to the same procedure. Being liquid at 25 °C, the required volume of ϵ-CL was added into the reactor with a previously flamed syringe. PCL was stopped by addition of an excess of HCl. PolyOPD precipitated as a white powder during polymerization. Poly-ϵ-CL was precipitated after polymerization by pouring the reaction medium into a large excess of heptane. Polymer was recovered by filtration, abundantly washed with cold methanol, and dried in vacuo at room temperature up to a constant weight.

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Table 1. Copolymerization of ϵ-CL with OPD Initiated by $Sn(Oct)_2$ in Toluene at 90 °C[a]

entry	[monomers] (M)	f_{OPD}[b]	conv (%)	F_{OPD}[c]
1	4	0	97	0
2	4	0.36	92	0.29
3	4	0.41	85	0.41
4	4	0.56	95	0.50
5	4	0.73	88	0.77
6	3	1	95	1

[a] Monomer to initiator molar ratio = 100; copolymerization time = 21 h. [b] Molar fraction of OPD in the comonomer feed. [c] Molar fraction of OPD in the copolymer, determined by ^{1}H NMR spectroscopy.

In a typical experiment of ϵ-CL/OPD copolymerization, OPD (2.27 mmol) was weighed in a glovebox, placed in a flame dried flask, followed by ϵ-CL (4.56 mmol). $Bu_2Sn(OMe)_2$ (0.011 mmol) was added to the comonomer mixture, that was maintained under stirring in an oil bath at 110 °C for 5 min. HCl excess was added, followed by chloroform (15 mL). The final solution was poured into heptane (150 mL) and the copolymer was precipitated, filtered, washed with cold methanol and dried.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25 °C. Copolymer composition (F_{OPD}) was determined by ^{1}H NMR from the relative intensity of the methylene signal of PCL at 4.08 ppm and the methylene signal of polyOPD at 4.35 ppm. PolyOPD and copolymers with OPD content higher than 50 mol % were solubilized in a solvent mixture of chloroform and trifluoroacetic acid (5/1; v/v).

Size exclusion chromatography (SEC) was performed in THF at 40 °C with a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector and a set of columns of different porosity: 10^5, 10^3, 500, and 100 Å. Molecular weight and molecular weight distribution of PCL were determined in reference to a universal calibration curve set up with the viscosimetric relationships for polystyrene and PCL in THF.[16]

Differential scanning calorimetry (DSC) was carried out with a Dupont 910 DSC thermal analyzer calibrated with indium. DSC measurements were performed at a scan rate of 10 °C/min under nitrogen with samples of ca. 10−15 mg.

Glass transition temperature (T_g) was measured with a Rheometrics ARES rheometer equipped with 8 mm diameter parallel plates and a transducer operating at −100 °C. The temperature was scanned at a 5 °C/min rate. The angular frequency was 1 Hz, the maximum strain 0.03%, and the applied force 100 g. T_g was reported as the maximum of the loss angle (tan δ) curve.

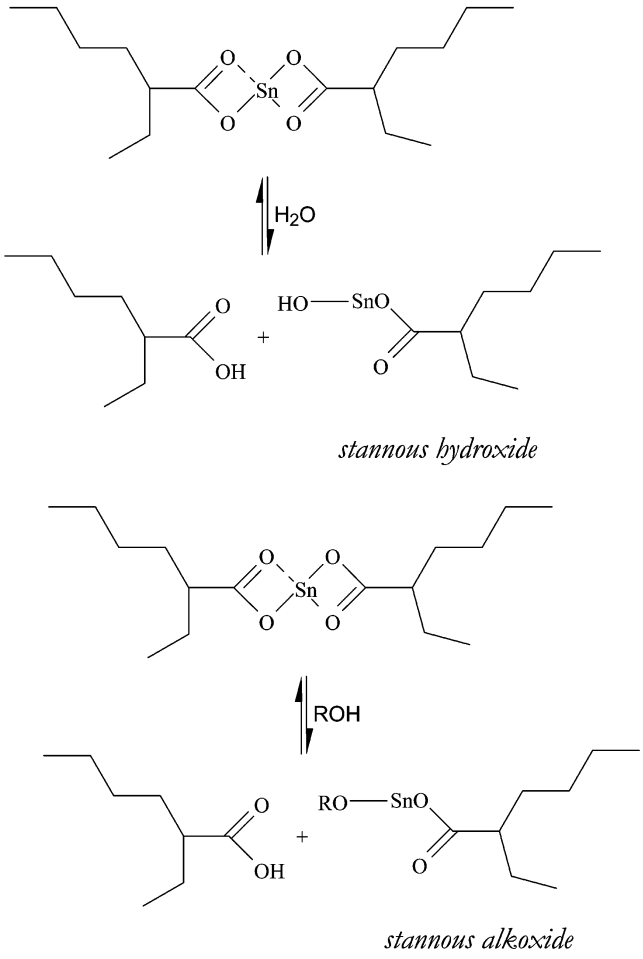
Results and Discussion

Initiation of the ϵ-CL/OPD Copolymerization. Copolymerization of ϵ-CL and OPD has been initiated by the metal compounds most commonly used in the ring-opening polymerization (ROP) of cyclic (di)esters, i.e., tin octanoate, dibutyltin dimethoxide, and aluminum isopropoxide.

Being intrinsically inactive toward ϵ-CL and OPD, tin octanoate must be used in combination with a protic compound. Whenever no compound of this type is added on purpose, adventitious water or hydroxylated impurities are the precursors of active stannous alkoxide and/or hydroxide as shown in Scheme 1.[17,18]

The occurrence of the copolymerization reaction in the presence of tin octanoate has been assessed by ^{1}H NMR analysis of the collected polymer. Signals characteristic of both the monomeric units are observed in agreement with the peak assignment shown in Figure 1. Some additional peaks of a low intensity in the alkene region is the signature of a limited degradation, as will be detailed in a forthcoming paper (random chain scission into shorter chains end-capped by carboxylic acid and vinyl groups).[19]

Scheme 1. Hydrolysis/Alcoholysis Reaction of Tin Octanoate



The series of copolymerization listed in Table 1 shows that the comonomer conversion may be higher than 85% for 21 h in toluene at 90 °C. Copolymer composition (F_{OPD}) is close to the comonomer feed composition (f_{OPD}), except for entry 2. Copolyesters containing more than 50 mol % of OPD are not soluble in the solvents commonly used for SEC analysis.

The randomness of the copolymerization has been assessed by ^{13}C NMR analysis in $CDCl_3$.[20] Indeed, four resonance peaks are observed in the ester carbonyl region[21] of the ^{13}C NMR spectrum (i.e., 150−185 ppm), which are characteristic of the expected diads with ϵ-CL (Figure 2). This sensitivity of the resonance of the ester carbon of each comonomer unit to the sequence effect, i.e., to the neighboring ester groups (ϵ-CL or OPD), confirms that the comonomer distribution is random.

This initiating system is however of a limited application because copolymerization at higher comonomer to initiator molar ratio (M/Sn > 300) failed, the purpose being not only to increase the chain length but also to decrease the copolymer contamination by residual tin. Indeed, low comonomer conversion is observed even when an alcohol is added as a co-initiator and for exceedingly long reaction time (>1 week).[22] It is therefore a problem to increase the chain length and to decrease the copolymer contamination by residual tin.

In contrast to tin octanoate, dibutyltin dimethoxide is an initiator for the ROP of cyclic (di)esters by the

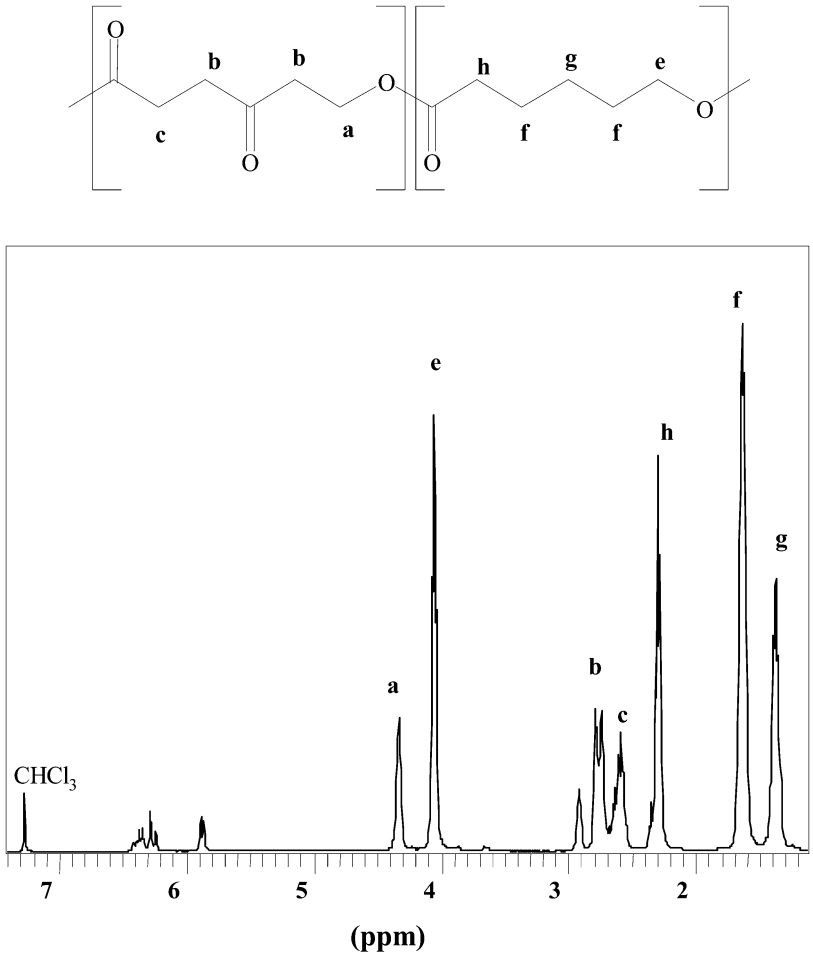


Figure 1. ^{1}H NMR spectrum for a ϵ-CL/OPD random copolyester (Table 1, entry 2).

Table 2. Bulk Copolymerization of ϵ-CL and OPD Initiated by $Bu_2Sn(OMe)_2$ at 110 °C

entry	M/Sn[a]	f_{OPD}[b]	time (min)	yield (%)	F_{OPD}[c]
1	600		5	94	
2	600	0.09	5	95	0.09
3	600	0.18	5	95	0.17
4	600	0.30	5	97	0.30
5	600	0.65	10	92	0.72

[a] M/Sn = 600 corresponds to a theoretical molecular weight of 36 000 g mol^{-1} at complete comonomer conversion. [b] Molar fraction of OPD in the comonomer feed. [c] Molar content of OPD in the copolymer determined by ^{1}H NMR spectroscopy.

traditional coordination−insertion mechanism. Being, however, a transesterification reaction catalyst,[23] $Bu_2Sn(OMe)_2$ commonly forms polyesters with a broad molecular weight distribution.[24] Mixtures of ϵ-CL and OPD of various compositions have been bulk polymerized by $Bu_2Sn(OMe)_2$ at 110 °C (Table 2). The reaction is very fast, as assessed by the medium viscosity, which is so high within less than 2 min that the magnetically driven stirring is no longer effective. Moreover, the comonomer conversion exceeds 90% within few minutes, and the copolymer composition (F_{OPD} as measured by ^{1}H NMR) is close to the composition of the comonomers feed (f_{OPD}). ^{13}C NMR spectra are similar to those ones recorded for copolyesters prepared in the presence of $Sn(Oct)_2$, which indicates that the randomness of the ϵ-CL/OPD copolymerization is maintained, when initiated by tin alkoxide at high temperature.

Kinetics of the OPD/CL copolymerization initiated by $Bu_2Sn(OMe)_2$ has been studied in bulk at 80 °C for a 30/70 comonomer feed (Table 3). Table 3 shows that copolymerization is fast (conversion higher than 90% within 10 min).

The average length of the two types of monomer sequence, i.e., L_{CL} and L_{OPD}, changes with the copolymerization time. These lengths were calculated from the integration of the diad signals recorded by ^{13}C NMR (eqs 1 and 2)

$$L_{CL} = I_{III}/[0.5(I_{II} + I_{IV})] \quad (1)$$

$$L_{OPD} = I_I/[0.5(I_{II} + I_{IV})] \quad (2)$$

where I_i is the intensity of peak i for the parent sequence. The molar fraction of OPD in each copolymer was calculated by eq 3:

$$F'_{OPD} = L_{OPD}/(L_{OPD} + L_{CL}) \quad (3)$$

The F'_{OPD} data agree with the ones measured by ^{1}H NMR. The copolyesters formed at low conversion contains more OPD than the comonomer feed (entry 1, Table 3). At higher conversion, the molar content of OPD in the copolymer and the comonomers feed are in agreement. OPD is thus slightly more reactive than ϵ-CL, and the randomness of the copolyester is not ideal. L_{CL} and L_{OPD} are expected to change beyond the copolymerization completion in the case of intermolecular transesterification. F_{OPD} is constant over a long reaction time (10−90 min), although the comonomers conversion increases very slowly from 93 to 99% during

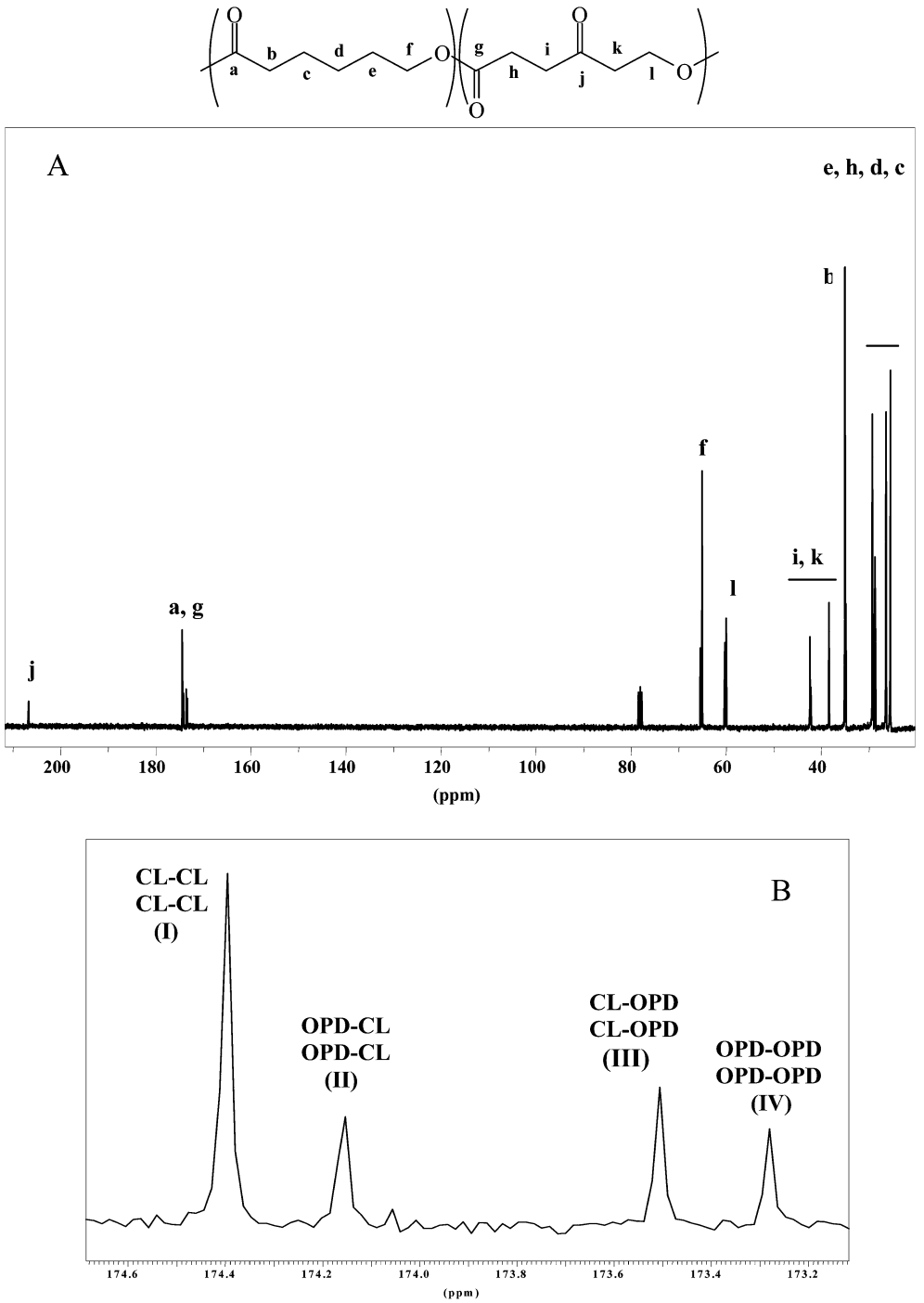


Figure 2. (A) ^{13}C NMR spectrum for a ϵ-CL/OPD random copolyester. (B) Expanded ^{13}C NMR spectrum in the carbonyl region (Table 1, entry 1).

Table 3. Bulk Copolymerization of CL with OPD Initiated by Dibutyltin Dimethoxide at 80 °C[a]

entry	time (min)	yield (%)	F_{OPD}[b]	L_{CL}	L_{OPD}	F'_{OPD}[c]	T_m (°C)	ΔH_m (J g^{-1})[d]
1	2	46	0.55	1.86	2.18	0.54	114	67
2	4	85	0.32	3.68	1.89	0.34	92	53
3	10	93	0.31	4.37	1.87	0.30	86	50
4	20	94	0.31	4.11	1.86	0.31	89	53
5	40	96	0.30	4.29	1.72	0.29	87	53
6	90	99	0.29	4.38	1.74	0.28	86	54

[a] Monomer to initiator molar ratio = 600. Molar fraction of OPD in the comonomer feed = 0.30. Theoretical molecular weight = 36 000 g mol^{-1}, at complete comonomer conversion. [b] Molar content of OPD in the copolymer (^1H NMR analysis). [c] Molar content of OPD in the copolymer (^{13}C NMR analysis). [d] DSC carried out under N_2 at 10 °C/min. Pretreatment: heating from −80 to 120 °C (160 °C, for entries 5 and 6), followed by quenching with liquid N_2. T_m and ΔH_m (DSC data) were reported for the second heating run.

this period of time (Table 3). In parallel, T_m and ΔH_m are also unchanged.

Aluminum isopropoxide [Al(O^{i}Pr)$_3$] is by far the most commonly used initiator of ROP of a large series of

Table 4. Copolymerization of ϵ-CL and OPD Initiated by Al(O^{i}Pr)$_3$ in Toluene at 90 °C[a]

entry	M/Al[c]	f_{OPD}[b]	yield (%)	$M_{n,PMMA}$ (K)[e]	MWD	F_{OPD}
1	500	0	99	98	1.9	0
2	400	0.05	4			
3	400	0.05	38[d]	7	1.3	0.01
4	400	0.15	4			
5	400	0.52	6			

[a] Comonomer concentration = 2 M; reaction time = 24 h. [b] Molar content of OPD in the comonomer feed. [c] Comonomer to aluminum molar ratio (M/Al) = 400, i.e., a theoretical molecular weight of 46 000 g mol^{-1} at complete conversion. [d] Reaction time = 1 week. [e] K stands for thousand.

Table 5. Synthesis of Low Molecular Weight Copolyesters of ϵ-CL and OPD Initiated by Al(O^{i}Pr)$_3$ in Toluene at 90 °C[a]

entry	1	2	entry	1	2
f_{OPD}	0.15	0.25	F_{OPD}	0.16	0.18
M/Al	86	85	$M_{n,^1H\ NMR}$[b]	9K	8K
yield (%)	3.3K	2.3K	$M_{n,SEC,THF}$[c]	3K	3.5K
$M_{n,theo}$	10K	10K	MWD	1.3	1.4

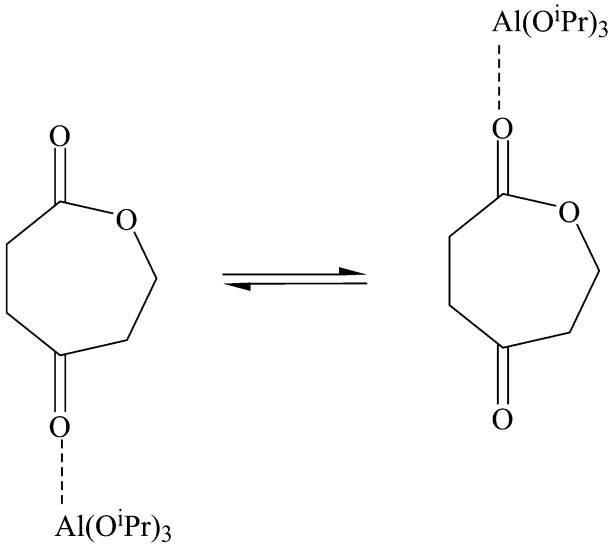
[a] Comonomer concentration = 1.2 M; reaction time = 6 days. [b] Determined by ^{1}H NMR analysis of the end groups. [c] Poor solubility in THF. K stands for thousand.

cyclics, e.g., ϵ-CL, lactides and glycolide, β-propiolactone, δ-valerolactone, 1,5-dioxanone, β-butyrolactone, adipic anhydride, and trimethylene carbonate.[25−32] In a first series of experiments, copolymers of high molecular weight (∼40 000 g mol^{-1}) and different OPD contents were targeted in toluene at 90 °C.

Table 4 shows that as soon as a small amount of OPD (5 mol %) is added to ϵ-CL, the comonomer conversion falls down dramatically (comparison of entries 2 and 3 with entry 1). Indeed, only 4% conversion is then observed under the conditions required for the ϵ-CL polymerization to be quantitative (24 h). However, when the reaction time is increased from 24 h to 1 week, the conversion is no longer negligible (38%) and the polydispersity index is rather low (1.3). Nevertheless, only 1 mol % OPD has been incorporated into the chains compared to 5 mol % in the original solution. These observations indicate that OPD has a very deleterious effect on the ROP kinetics of ϵ-CL when Al is substituted for Sn. Al might interact with the carbonyl of OPD to the point where coordination of ϵ-CL to the metal is dramatically hindered and the general kinetics is decreased. Therefore, in a second series of experiments, the OPD to aluminum molar ratio has been decreased and the reaction time has been increased from 1 day to ca. 1 week (Table 5).

Copolymerization remains however slow, molecular weight is higher than expected, and the rather narrow molecular weight distribution might be only apparent, because copolymer that contains ca. 15 mol % OPD has a limited solubility in THF, thus making SEC analysis unreliable.

Scheme 2. Competitive Coordination of Al(O^{i}Pr)$_3$ with the Ketone and the Ester Functions of 2-Oxepane-1,5-dione



Effect of Cyclohexanone on Polymerization of ϵ-Caprolactone. To confirm that OPD (particularly the ketone carbonyl of it) can perturb the course of the ϵ-CL polymerization, cyclohexanone was added to the polymerization medium (Table 6). The effect strongly depends on the initiator used, even for tin-containing initiators. Indeed, cyclohexanone slows down ROP of ϵ-CL co-initiated by tin octanoate (entries 1−3). The copolymerization yield drops from 67% to 38% when the carbonyl to Sn molar ratio (C═O/Sn) is 100 (entry 2), which mimics a copolymerization experiment with f_{OPD} = 0.22. This effect is amplified when more cyclohexanone is used as shown by a comonomer conversion of 25% at a C═O/Sn ratio of 500 (mimicking f_{OPD} = 0.58; entry 3). Moreover, M_n decreases and the apparent molecular weight distribution remains narrow (1.1−1.2). Although cyclohexanone has a deleterious effect on ROP of ϵ-CL in the presence of tin octanoate, the situation changes deeply whenever $Bu_2Sn(OMe)_2$ is the initiator. Then, the polymerization course is unaffected by cyclohexanone as shown by unchanged conversion, M_n, and M_w/M_n even up to a 500 molar excess of this ketone with respect to Sn (entries 4−6). Perturbation is noted again when ROP of ϵ-CL is initiated by Al(O^{i}Pr)$_3$ even at a low cyclohexanone to Al molar ratio (C═O/Al: 20),

Table 6. Effect of Cyclohexanone on the ϵ-CL Polymerization Initiated/Catalyzed by Al(O^{i}Pr)$_3$, Sn(Oct)$_2$, and $Bu_2Sn(OMe)_2$ in Toluene (No OPD Present in the Medium)[a]

entry	initiator	C═O/Al	time (h)	yield (%)	M_n (K)[e]	MWD
1	Sn(Oct)$_2$[b]		4	67	15	1.1
2	Sn(Oct)$_2$[b]	100	4	38	9.5	1.1
3	Sn(Oct)$_2$[b]	500	4	25	4	1.2
4	$Bu_2Sn(OMe)_2$[c]		5	93	20	1.5
5	$Bu_2Sn(OMe)_2$[c]	100	5	92	19	1.6
6	$Bu_2Sn(OMe)_2$[c]	500	5	94	18	1.4
7	Al(O^{i}Pr)$_3$[d]		0.25	86	10.5	1.3
8	Al(O^{i}Pr)$_3$[d]	2	0.25	88	10	1.3
9	Al(O^{i}Pr)$_3$[d]	20	0.25	80	18	1.3
10	Al(O^{i}Pr)$_3$[d]	200	0.25	45	0.4	2.8

[a] Polymerization temperature = 25 °C, except when Sn(Oct)$_2$ is used. [ϵ-CL]$_0$ = 0.9 M. [b] Reaction temperature = 100 °C. 1-Butanol is used as a co-initiator (1-butanol to Sn molar ratio = 2). Theoretical M_n at complete conversion is 22 000 g mol^{-1}. [c] Theoretical M_n at complete conversion is 22 000 g mol^{-1}. [d] Theoretical M_n at complete conversion is 12 000 g mol^{-1}. [e] K stands for thousand.

Table 7. Melting Temperature, Glass Transition Temperature, and Enthalpy of Melting for (Co)polymers of ϵ-CL and OPD[a]

entry	F_{OPD}	T_m (°C)[b]	T_g (°C)[c]	ΔH_m (J g^{-1})[b]
1	0	59	−65	71
2	0.09	64	−55	55
3	0.17	69	−49	51
4	0.30	94	−40	52
5	0.55	114	−19	67
6	0.72	137	−1	75
7	1	151	37[d]	93

[a] Monomer-to-initiator ratio (M/Sn) = 600. Bulk (co)polymerization initiated by dibutyltin dimethoxide at 110 °C except for polyOPD (entry 7) that was prepared in toluene at 100 °C with $[OPD]_0 = 1$ M. [b] DSC carried out under N_2 at 10 °C/min. Pretreatment: heating from −80 to 120 °C (160 °C, for entries 5 and 6) followed by quenching with liquid N_2. T_m and ΔH_m (DSC data) were reported for the second heating run. [c] T_g was determined by dynamic mechanical analysis. [d] T_g was determined by DSC.

Table 8. Dependence of the Distance between Two Neighbor Macromolecules and the OPD Content

entry	F_{OPD}[a]	δ (Å)[b]	entry	F_{OPD}[a]	δ (Å)[b]
1	0	2.98	4	0.72	2.85
2	0.17	2.89	5	1	2.82
3	0.30	2.88			

[a] Molar content of OPD in the copolymer. [b] δ = distance between two neighbor macromolecules.

which mimics copolymerization with $f_{OPD} = 0.02$. Although estimated by SEC, M_n is much higher than the expected value (comparison of entries 7 and 9), consistent with a lower number of initiating species in the medium. The situation is worst when the C═O/Al ratio is further increased (entry 10); because the apparent conversion is significantly decreased, the molecular weight is very low and the molecular weight distribution is broad and multimodal. So, the effect of cyclohexanone (and supposedly of OPD) on the ϵ-CL polymerization strongly depends on the amount which is used. At very low content ($f_{OPD} < 0.001$), no effect is noted, whereas the polymerization kinetics is slightly decreased and M_n is increased notably when the amount of cyclohexanone is 2 mol % with respect to ϵ-CL. Finally, the ϵ-CL polymerization is very slow, and only very short chains (oligomers) are formed with a high polydispersity in the presence of 200 times more cyclohexanone than Al, i.e., 14 mol % with respect to ϵ-CL. The very low efficiency of $Al(O^iPr)_3$ as initiator of the ϵ-CL/OPD copolymerization can be rationalized as follows. The ϵ-CL/OPD copolymerization is thought to be affected by a competition between the ketone and the ester of ϵ-CL (and OPD) for coordination to Al (Scheme 2). At very high contents of ketone compared to $Al(O^iPr)_3$, the copolymerization might be inhibited because the equilibrium shown in Scheme 2 would be strongly shifted to the left. The same kind of competition for coordination to the metal might account for unsuccessful attempts of ϵ-CL/OPD copolymerization initiated by yttrium isopropoxide, titanium isopropoxide, and scandium triflate.[22] It is worth pointing out that the coordination of a ketone (Lewis base) to aluminum alkoxide (Lewis acid) is the very first step in the mechanism of the well-known Meerwein−Verley−Ponndorff reduction of ketones into alcools.[33] Nevertheless, no reduction of the ketone of OPD has been detected by ^{1}H NMR under the conditions used in this work.

Melting and Glass Transition Temperature (T_g) of Random Copolyesters of ϵ-Caprolactone and 2-Oxepane-1,5-dione. Table 7 shows that copolyesters prepared by initiation with dibutyltin dimethoxide are semicrystalline whatever their composition (Table 7). A single melting temperature is observed between 59 °C (poly ϵ-CL) and 151 °C (polyOPD).

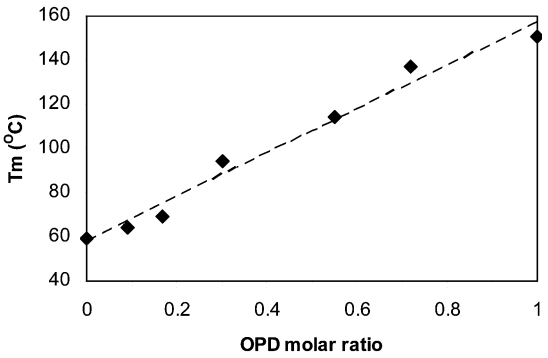


Figure 3. Plot of T_m vs OPD content for copolymers prepared by ring-opening polymerization initiated by dibutyltin dimethoxide.

Figure 3 shows the composition dependence of the melting temperature, T_m, of the copolyesters measured by DSC during the second temperature scan. A linear dependence consistent with a cocrystallization phenomenon is unusual compared to other copolyesters of ϵ-CL with comonomers such as L-lactide and glycolide.[5,9] It has never been reported for ϵ-CL and cyclic (di)ester copolymers, at least to our best knowledge. One example is known, however, for ϵ-CL-containing copolyesteramides, i.e., copolymers of ϵ-CL/caprolactam and ϵ-CL/laurolactam.[6,7] Cocrystallization results from an isomorphic replacement in the crystal lattice of the copolyester. Indeed, WAXS analysis reveals that polyOPD and poly ϵ-CL have the same crystal structure. The unit cell is orthorhombic and perpendicular to the chain direction.[34] Moreover, the distance between two neighbor molecules in the copolyesters lies between 2.98 Å (poly ϵ-CL) and 2.82 Å (polyOPD) and decreases regularly with the OPD content (Table 8). This observation suggests an increase of the intermolecular interactions when OPD is part of the copolyester in agreement with a higher melting temperature for the copolyesters compared to poly ϵ-CL.

The melting enthalpy (ΔH_m) listed in Table 7 depends on the copolymer composition, although in a nonmonotonic way. T_g regularly increases with the OPD content as shown in Figure 4 together with the theoretical prediction by the Fox equation (eq 4)

$$1/T_g = (\omega_1/T_{g1}) + (\omega_2/T_{g2}) \quad (4)$$

where ω_i and T_{gi} are the weight content for compound i and T_g for the parent homopolymer, respectively.[2]

The apparent validity of the Fox equation (within the limits of experimental errors) indicates that the composition of the amorphous phase (ω_I) may be approximated to the overall composition determined by ^{1}H NMR.

Conclusions

Random copolyesters of ϵ-CL and OPD have been prepared by bulk ring-opening copolymerization initiated by dibutyltin dimethoxide at 110 °C. Conversion is complete within 5 min for chains with a theoretical molecular weight of 36 000 g mol^{-1} and OPD content of 30 mol % or less. Randomness of the copolymers has

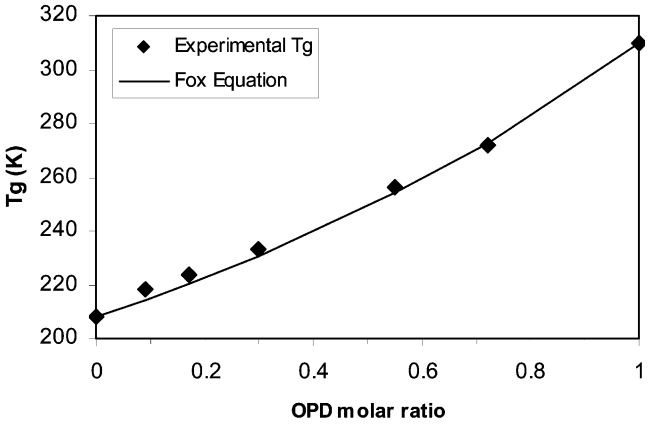


Figure 4. Plot of T_g vs OPD content for copolymers prepared by ring-opening polymerization initiated by dibutyltin dimethoxide.

been confirmed by NMR analysis, whereas solubility in THF decreases with increasing OPD content. Tin octanoate and aluminum isopropoxide have proved to be of a very low efficiency in promoting the copolymerization within a reasonable period of time. The reason for this kinetic problem has to be found in the preferential coordination of the metal by the ketone of OPD rather than by the ester carbonyl of the comonomers which are no longer activated as required by the coordination−insertion mechanism. It turns out that initiators based on low oxophilic metals are better suited for OPD ring-opening polymerization, although oxidation number and steric hindrance may also play a major role.

The ϵ-CL/OPD copolyesters are semicrystalline over the whole composition range. The melting temperature linearly increases with the OPD content as result of the cocrystallization of the ϵ-CL with OPD counits. Moreover, DSC analysis has shown that T_g is in accordance with the Fox equation. Therefore, the thermal transitions (T_m and T_g) of the copolyesters are directly controlled by their composition. The effect of the OPD content on the biodegradability and thermal stability of poly-ϵ-CL will be reported in a forthcoming paper.

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