Electronic Supplementary Information (ESI)

Preparation of 3-PPD. 3-Phenoxypropyl-1,4-dioxanium hexafluoroantimonate (**3-PPD**) were synthesized under argon in the glove box by reaction of silver hexafluoroantimonate (0.373g, 1.085 mmol) with **3-PPBr** (0.212g, 0.987mmol) and 60 mL of 1,4-dioxane used as solvent. AgBr precipitated immediately. Because 1,4-dioxanium salts cannot be prepared under rigorous exclusion of moisture, 2,6-di-t-butyl-pyridine (0.208g, 1.085 mmol) was used as a non-nucleophilic proton trap in order to neutralize the acid produced during the reaction between cationic species and the trace of molecule of water. The solution was stirred for at least 3 hours. [7]

Polymerization procedure. Because the ring opening reaction of oxetane is an exothermic process ($\Delta H° = 80.8$ kJ mol^{-1} (19.3 $kcal.mol^{-1}$) at -9 °C in methyl chloride), [5] it was possible to monitor the reaction calorimetrically. A modification of the technique of Biddulph and Plesch was used.[4] In a typical experiment, 25 ml of oxetane in 1,4-dioxane were thermostatted at 35°C under argon. The water from the thermostat bath at 35°C was continually passed through the outer double jacket. When the system was balanced to 35°C, 1.9 ml of catalyst was injected into the calorimeter by means of a bleed valve system.[4] Samples of the polymerization solution were taken using an anaerobic sampling technique and then quenched by a solution of 10^{-2} M of sodium hydroxide in water. After addition of 30 ml of dichloromethane, the quenched reaction mixture was sequentially washed with water to neutralize the pH and to remove the initiator residues and salts. The dichloromethane sample containing the polymer was then dried over $MgSO_4$. The dried polymer was filtered off and the filtrate washed with dry dichloromethane. The polymer was recovered from the organic layer by removal of the solvent to constant weight. Yield = 1.5 g

Molecular structure by NMR spectroscopy. ^{1}H NMR spectra were recorded on a Bruker AC 300, and were measured in $CDCl_3$ solution at room temperature. For ^{13}C NMR analysis the P.E.N.D.A.N.T pulse technique was used, which ensures methyl and methine carbons appear as positive peaks and methylene and quaternary carbon atoms as negative peaks.

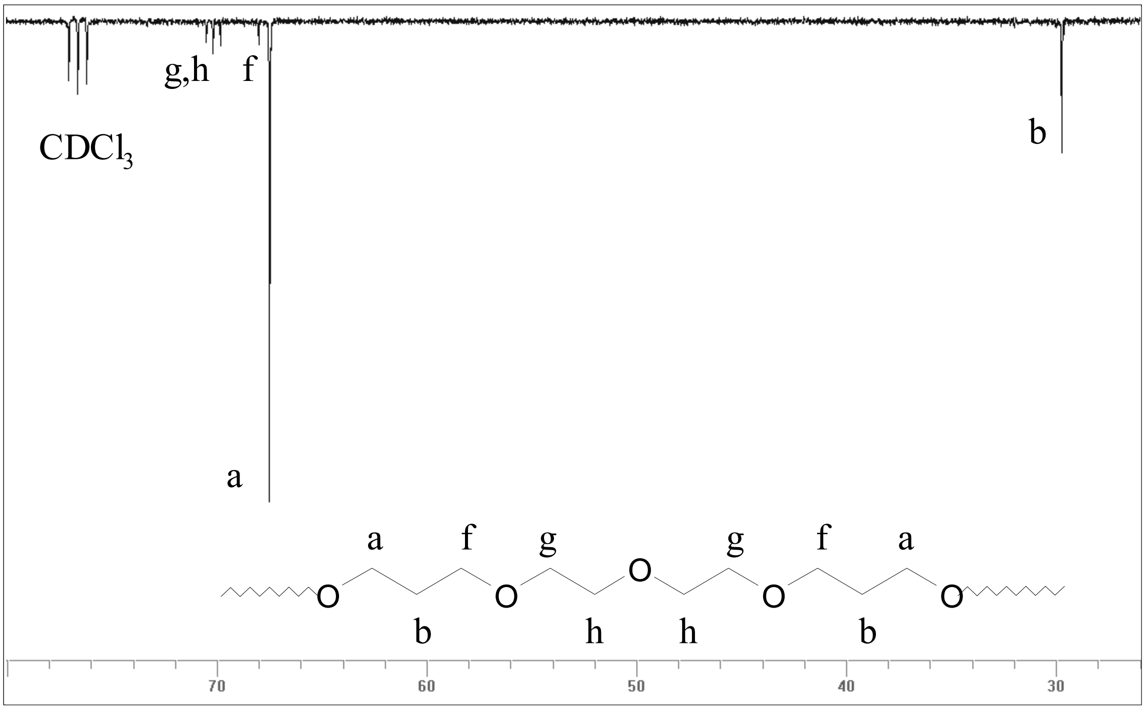

Fig. S1 ^{13}C NMR spectrum of poly(oxetane-co-(1,4-dioxane)) obtained in 1,4-dioxane at 35 °C using 3-PPD as initiator.

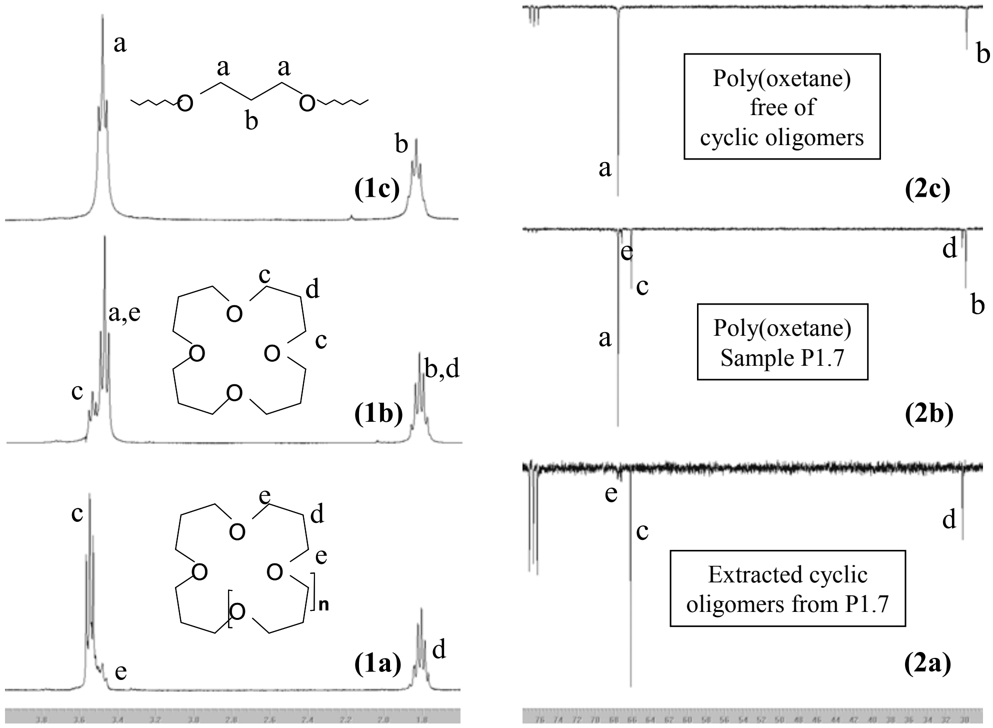

Fig. S2 (1) and (2) represent respectively the ^{1}H and ^{13}C NMR spectrum of poly(oxetane) obtained in dichloromethane using BF_3:MeOH as initiator (c) before and (b) after extraction of low molecular weight cyclic oligomers materials (a).

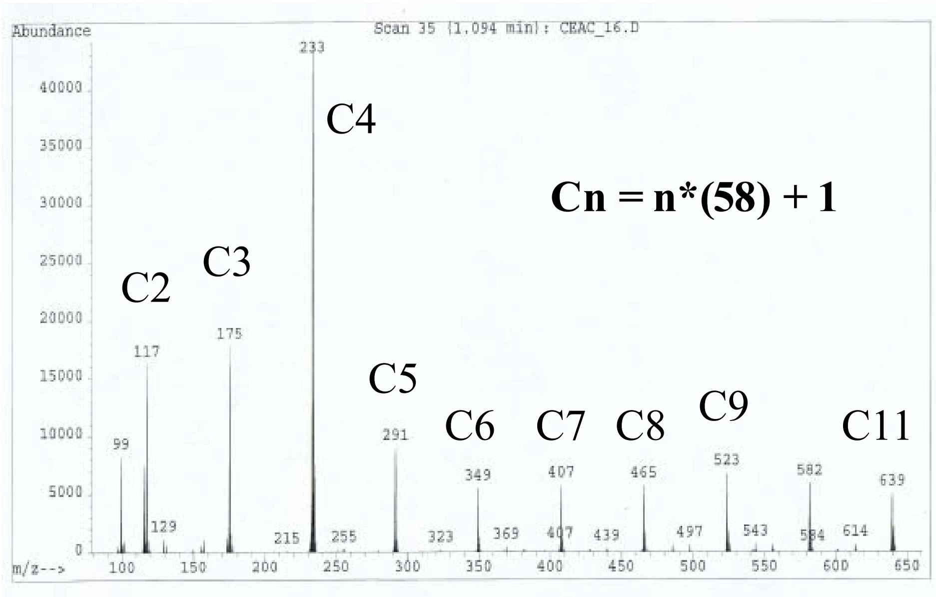

Fig. S3 Masse Spectrum of low cyclic oligomers materials extracted with cyclohexane.

Table 1 ^{1}H and ^{13}C chemical shift δ (ppm) of $-CH_2-$ group in poly(oxetane) and poly(oxetane-co-1,4-dioxane).

	Structure	Peak [j]	Chemical shift [a]	
			^{13}C NMR	^{1}H NMR
			δ (ppm)	δ (ppm)
chains	$O\mathit{CH_2}CH_2\mathit{CH_2}O$ [k]	(a)	67.49	**t:** 3.46, 3.48 and 3.50
	$OCH_2\mathit{CH_2}CH_2O$ [k]	(b)	29.76	**q:**1.78, 1.80, 1.82, 1.84, 1.87
	$OCH_2CH_2CH_2OCH_2\mathit{CH_2}O\mathit{CH_2}CH_2OCH_2CH_2CH_2O$ [n]	(g)	70.23 [n]	peaks from 3.46 to 3.6 [p]
	$OCH_2CH_2CH_2O\mathit{CH_2}CH_2OCH_2\mathit{CH_2}OCH_2CH_2CH_2O$ [n]	(h)	69.85 [n]	peaks from 3.46 to 3.6 [p]
	$OCH_2CH_2\mathit{CH_2}OCH_2CH_2OCH_2CH_2O\mathit{CH_2}CH_2CH_2O$ [n]	(f)	68 [n]	peaks from 3.46 to 3.6 [p]
	$O\mathit{CH_2}CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2\mathit{CH_2}O$ [n]	(a)	67.49 [n]	peaks from 3.46 to 3.6 [p]
	$OCH_2\mathit{CH_2}CH_2OCH_2CH_2OCH_2CH_2OCH_2\mathit{CH_2}CH_2O$ [n]	(b)	29.76 [n]	peaks from 3.46 to 3.6 [p]
Ring [m]	$O\mathit{CH_2}CH_2\mathit{CH_2}O$ (small cyclic oligomers) [m]	(c)	66.07	**t:**3.56, 3.54, 3.52
	$O\mathit{CH_2}CH_2\mathit{CH_2}O$ (large cyclic oligomers) [m]	(e)	67.08	**t:** from 3.434 to 3.551 [p]
		(e)	67.44	**t:** from 3.434 to 3.551 [p]
	$OCH_2\mathit{CH_2}CH_2O$ (small cyclic oligomers) [m]	(d)	30.15	**q:**1.835, 1.815, 1.795, 1.775
	$OCH_2\mathit{CH_2}CH_2O$ (large cyclic oligomers) [m]	(d)	29.76	**q:** from 1.742 to 1.87 [p]

[a] $CDCl_3$ was used as solvent.

[j] symbols associated with the chemical shift in Fig. S1and S2.

[k] chemical shift obtained from NMR spectra of linear polymer free of cyclic oligomers. Fig. 2, spectra 1c and 2c.

[m] chemical shift obtained from NMR spectra of isolated cyclic oligomers. Fig. 2, spectra 1a and 2a.

[n] chemical shift obtained from ^{13}C NMR spectra of the sample P3.5. Fig. 2, spectra 1a and 2a.

[p] Peaks overlap

Gel permeation chromatography (GPC) analysis. Gel permeation chromatography was performed on a Knauer instrument using a differential refractometer as detector, and two gel columns supplied by (Polymer Laboratories) used in series, a 5μ-PL gel column with an exclusion limit of 10^3 Å and a mixed B column. THF was used as solvent. The system was calibrated with polystyrene standards

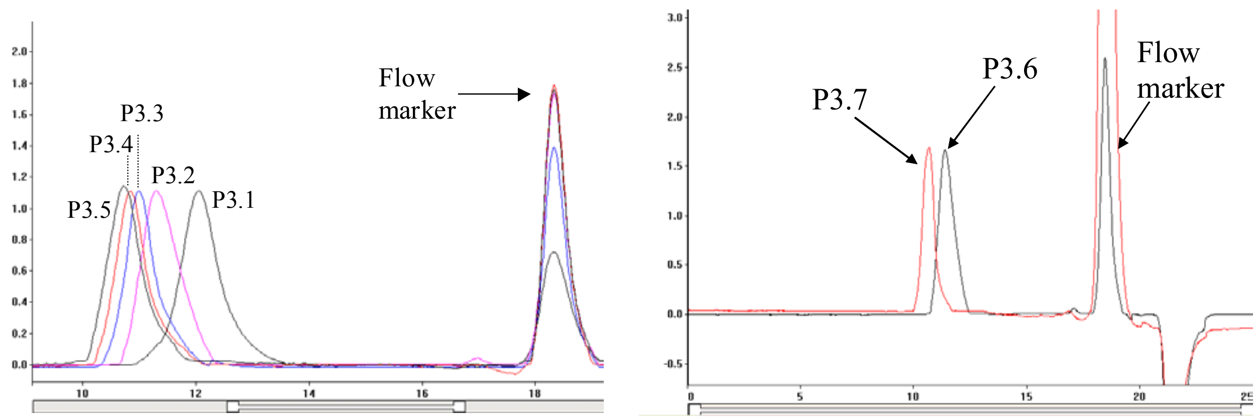

Fig. S4 GPC traces of polymer obtained throughout the polymerization (a) of 1.125 M of oxetane initiated by 0.00114 M of **3-PPD** in 1,4-dioxane at 35 ºC, series P3, (b) and after chain expansion polymerization of polyoxetane, polymer N. P3.7, obtained by addition of monomer solution onto active polymer solution, polymer N. P3.6, almost free of monomer issue from the polymerization of 1.125 M of oxetane by 0.002 M of **3-PPD** in 1,4-dioxane at 35 ºC.

Table 2 Results of the polymerization of 1.125 M of oxetane by 0.00114 M of **3-PPD** in 1,4-dioxane at 35 °C.

Polymer No	P [a]	$F_{1,4\text{-}D}$ [b] ^{13}CNMR	Time	Conversion	$M_{n\ th.}$ [d,e]	$M_{n\ GPC}$ [f]	PDI [f]
	%	%	Min	%	g.mol^{-1}	g.mol^{-1}	
P3.1	20.7	0	16	20.7 [a]	11,850 [d]	31,920	1.22
P3.2	37	0	34	37 [a]	21,190 [d]	51,700	1.18
P3.3	52.5	0	68	52.5 [a]	30,050 [d]	79,000	1.22
P3.4	73.45	0.4	145	73 [c]	41,840 [e]	98,000	1.26
P3.5	84.15	0.9	240	83 [c]	47,570 [e]	120,610	1.23

[a] Evaluation by gravimetric measurement. P = (Wgt $_{Polymer}$ / Wgt $_{Oxetane}$) x 100. Error ± 2 %

[b] Composition of the copolymer on the basis of ^{13}C NMR data. $f_{1,4\text{-}D} = S/(S+R) \times (100-f_{1,4\text{-}D})$ with $S = ((I_{70.23\text{-}69.85})/4 + I_{68}/2)$ and $R = ((I_{67.49}/2+I_{29.76})/2)$. See Table for ^{13}C NMR data.

[c] Conversion = $P \times (100 - g_{1,4\text{-}D})/100$ with $g_{1,4\text{-}D} = (f_{1,4\text{-}D} \times M_{1,4\text{-}D})/(f_{1,4\text{-}D} \times M_{1,4\text{-}D} + (100- f_{1,4\text{-}D}) \times M_{Oxetane}) \times 100$.

[d] $M_{n\ th.\ Pi,j} = (n_{Oxetane} / n_{Initiator}) \times M_{Oxetane} \times \text{conversion}_j$

[e] $M_{n\ th.\ Pi,j} = (n_{Oxetane} / n_{Initiator}) \times (M_{Ox} + M_{1,4\text{-}D} \times f_{1,4\text{-}D}) \times \text{conversion}_j$

[f] Determined by SEC calibrated with M_n values obtain from PS standard.

Table 3 Results of the addition of monomer solution on active polymer solution.

Polymer No.	$[I]_0$	$[Ox]_0$	$f_{1,4\text{-}D}$ [b] ^{13}CNMR	Conversion	$M_{n\ th.}$ [e]	$M_{n\ (GPC)}$ [f]	PDI [f]
	mol.L^{-1}	mol.L^{-1}	%	%	g.mol^{-1}	g.mol^{-1}	
P3.6	0.002	1.125	1.2	98[c]	31,845 [h]	79,500	1.24
P3.7	0.00187 [g]	1.11[g]	1	96[c]	67,115 [h]	160,100	1.2

[b c e f] Refer to Table 1

[g] Initial concentration of oxetane and initiator calculated after addition of monomer solution.