Supplementary Material (ESI) for Chemical Society Reviews
This journal is (c) The Royal Society of Chemistry 2009

Synthesis of Polycaprolactone: a review

Marianne Labet, Wim Thielemans*

Driving Innovation in Chemistry and Chemical Engineering

School of Chemistry and Process and Environmental Research Division-Faculty of Engineering, The University of Nottingham, University Park, NG7 2RD, United Kingdom

*Corresponding author: Wim.Thielemans@nottingham.ac.uk

Supporting Information

This supporting information combines a wide variety of systems used or tried to catalyse the ring-opening polymerisation of ε-caprolactone. Experimental systems are described as well as the appropriate references. Section 1 combines successful systems in the same sequence as addressed in the review. Section 2 addresses the systems that have been attempted for the ROP of ε-CL but did not lead to polymerisation, or low conversion or oligomers in the conditions used. This information is just as valuable as successful systems. Section 3 combines all reported catalysts in a periodic table as a quick reference. One can immediately see that the periodic table has already been well covered. References are listed at the end.

Section 1: Catalyst systems

ROP catalysed by metal-based compounds

1. Alkali-based catalysts

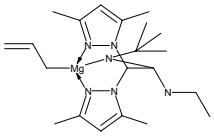
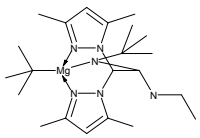
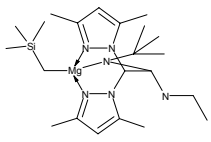
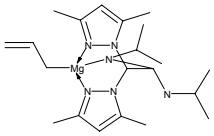
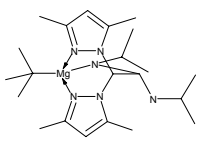
Table 1.1 - Conditions for the ROP of ε-CL using alkali-based catalysts, and characteristics of the resulting PCL

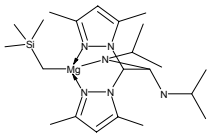
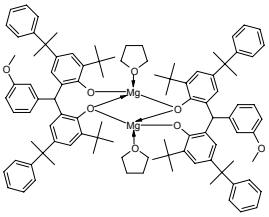
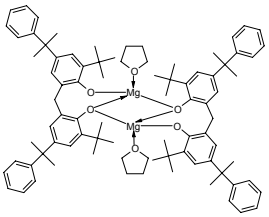
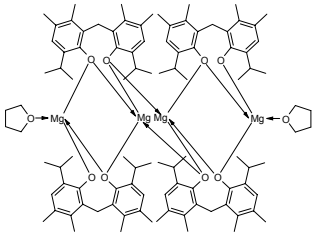
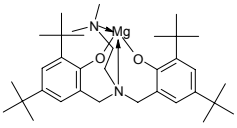
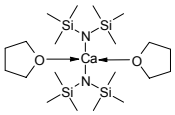
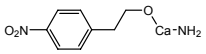
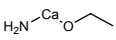
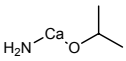
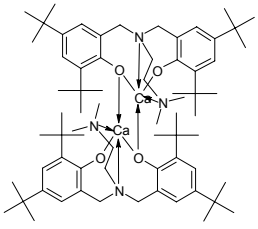
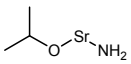
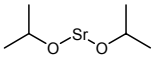
Entry	Catalyst/Initiator	solvent	[M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M_n (g/mol)	PDI	Ref
1		dioxane	50:1	25	5 min	100		5,700		[1]
2		none	100:1	180	120 min		89	77,000		[2]
3		none	250:1	20	10 min	93		12,100		[3]
		toluene	250:1	20	1 h	98		11,600		[3]
		benzene	250:1	20	1 h	96		10,700		[3]
4		toluene	49:1	110	15 min		35	17,500	2.0	[4]
		$scCO_2$ (155 bar)	49:1	108	15 min		7	6,000	2.0	[4]

$scCO_2$ = supercritical carbon dioxide
[M] = concentration of monomer (ε-CL); [C/I] = concentration of catalyst/initiator
M_n = number average molecular weight
PDI = polydispersity index

2. Alkaline earth-based catalysts

Table 1.2 - Conditions for the ROP of ε-CL using alkaline earth-based catalysts, and characteristics of the resulting PCL

entry	Catalyst *catalyst/initiator*	initiator	solvent	[M]:[C]:[I] [M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1			toluene	500:1	20	15 min		84	34,000[(w)]	1.16	[5]
2			toluene	500:1	20	15 min		96	47,000[(w)]	1.27	[5]
3			toluene	500:1	20	1 min		97	52,000[(w)]	1.41	[5]
				5000:1	20	5 min		57	112,000[(w)]	1.43	[5]
4			toluene	500:1	20	10 min		86	38,000[(w)]	1.21	[5]
5			toluene	500:1	20	10 min		97	51,000[(w)]	1.33	[5]

entry	Catalyst *catalyst/initiator*	initiator	solvent	[M]:[C]:[I] [M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
6			toluene	500:1	20	10 s		98	59,000$^{(w)}$	1.45	5
				5000:1	20	5 min		87	160,000$^{(w)}$	1.42	5
7			toluene	25:1:1	25	2 h	> 99		3,500$^{(n)}$	1.06	6
				200:1:1	25	2 h	97		5,600$^{(n)}$	1.06	6
				12.5:0.06:1	25	1 h	>99		1,400$^{(n)}$	1.10	6
8			toluene	50:1:1	40	12 h	92		5,450$^{(n)}$	1.08	6
				50:1:1	70	2 h	99		3,000$^{(n)}$	1.24	6
				100:1:1	70	4 h	90		11,400$^{(n)}$	1.13	6
				100:0.5:1	70	5 h	95		9,500$^{(n)}$	1.18	6
				450:1:1	110	12 h	99		54,200$^{(n)}$	1.35	6
9			toluene	25:0.5:1	56	30 min	99		2,000$^{(n)}$	1.11	7
			toluene	200:0.5:1	56	3 h	99		19,000$^{(n)}$	1.19	7
			toluene	25:0.1:1	56	1 h	99		3,300$^{(n)}$	1.06	7
			toluene	10:0.002:1	56	2 h	86		1,100$^{(n)}$	1.12	7
10			toluene	200:1	60	24 h	5.0				8
11			none	100:1	120	10 min	100		21,000$^{(n)}$	1.25	9
12a		none	toluene	100:1	~18	1 min	100		22,800$^{(n)}$	3.95	10
			THF	100:1	~18	8 min	100		11,800$^{(n)}$	2.39	10
12b			THF	50:0.5:1	~18	6 min	100		6,200$^{(n)}$	1.24	10
12c		—OH	THF	50:0.5:1	~18	10 min	100		9,000$^{(n)}$	1.29	10
				50:0.5:1	~18	6 min	81		12,800$^{(n)}$	1.15	9
13			toluene	10:1:1	70	12 h		87.2	2,400$^{(n)}$	1.20	11
14			xylene	650:1:1	70	3 h		92	103,000$^{(v)}$		12
15			xylene	650:1:1	70	3 h		90	90,000$^{(v)}$		12
16			toluene	200:1	60	12 h	40.1		26,000$^{(w)}$	1.3	8
17			toluene	89:1:1	41	2 h	100		30,300$^{(n)}$	1.85	13
				439:1:1	41	6 h	100		87,400$^{(n)}$	3.07	13
18			toluene	44:0.5:1	40	6 h	100		45,200$^{(n)}$	4.52	13
				78:0.5:1	40	6 h	99		59,900$^{(n)}$	7.37	13

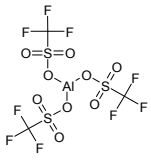
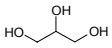
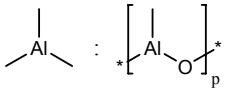
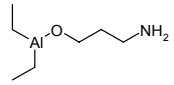
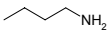
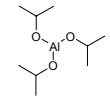
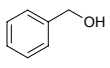
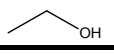
THF = tetrahydrofuran

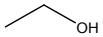
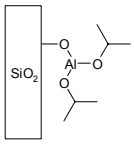
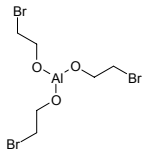
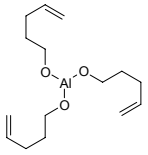
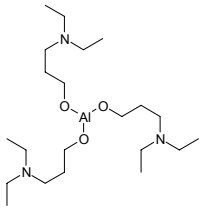
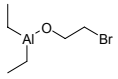
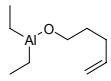
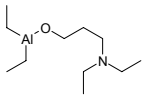
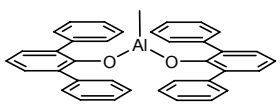
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
M = molecular weight
(n) = number average molecular weight, (v) = viscosimetric average molecular weight, (w) = weight average molecular weight
PDI = polydispersity index

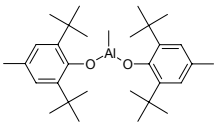
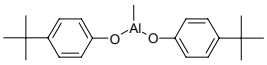
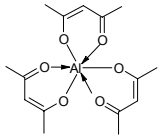
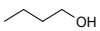
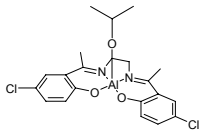
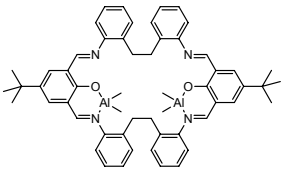
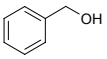
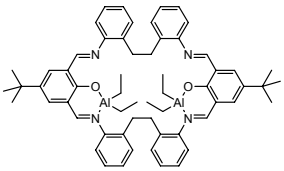
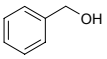
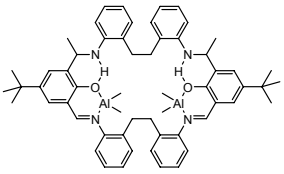
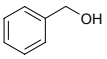
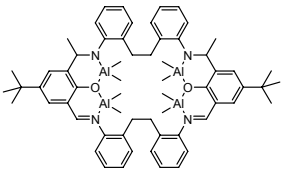
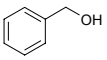
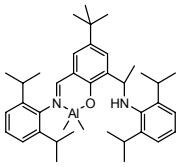
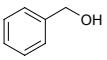
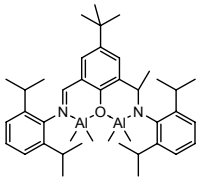
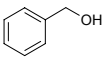
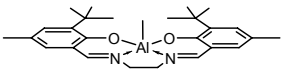
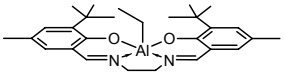
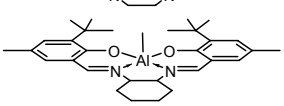
3. Poor metals-based catalysts

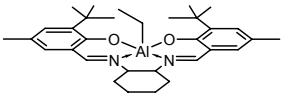
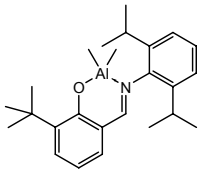
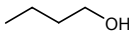
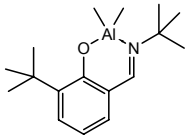
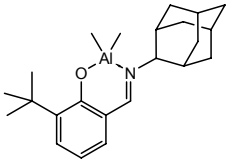
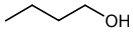
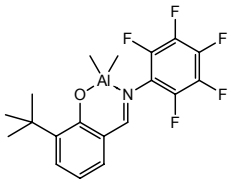
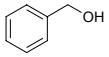
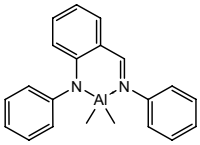
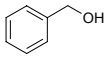
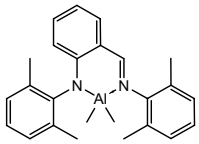
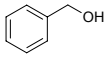
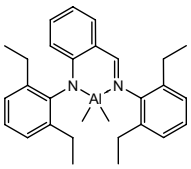
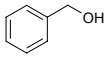
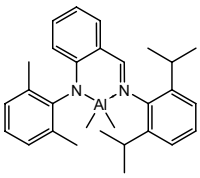
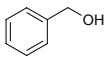
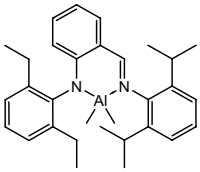
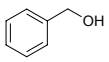
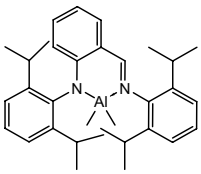
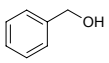
a. Aluminium-based catalysts

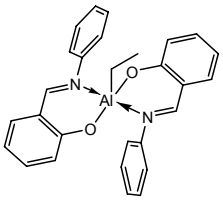
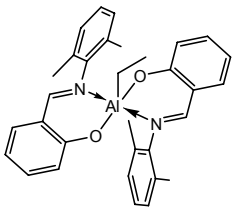
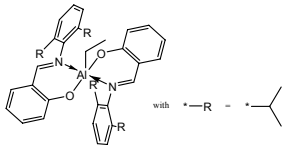
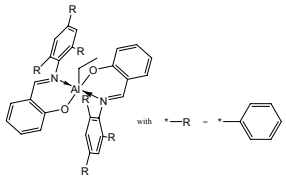
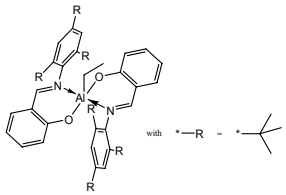
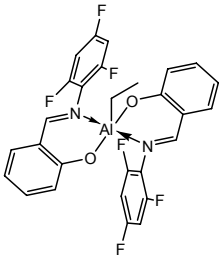
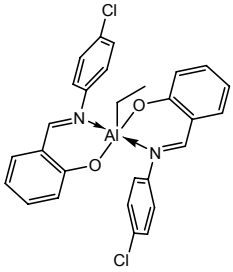
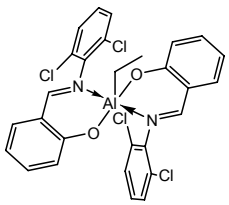
Table 1.3 - Selected conditions for the ROP of ε-CL using aluminium-based catalysts, and characteristics of the resulting PCL

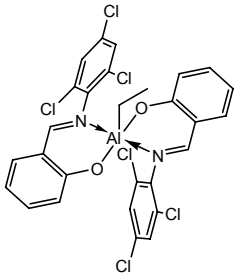
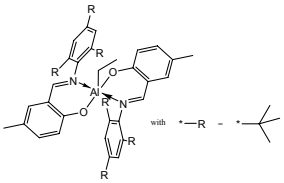
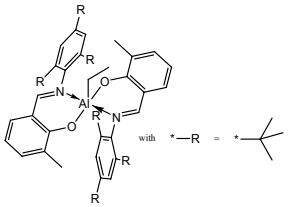
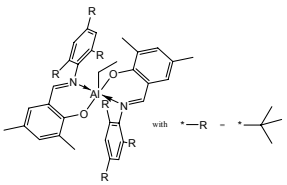
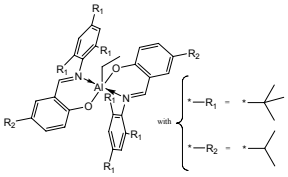
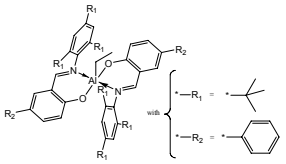
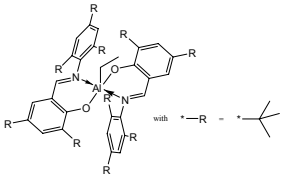
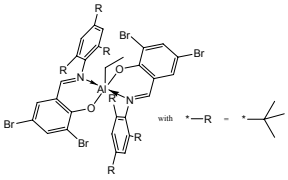
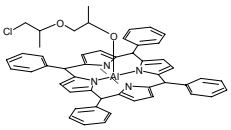
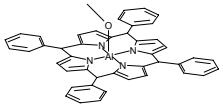
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
1			none[(a)]	120:0.3:1	60	6 h		89	18,400	1.94	14
2			DCM	50:0.3:1	RT	1 h	94		6,000	1.35	15
3	 90:10		toluene	25:1	60	20 h	89		2,900[(n)]		16
4			toluene		40		100				17
5			toluene	43:1:3	40	23 h	100		3,800	1.45	17
			THF	43:1:2	40	22 h	100		3,500	1.35	17
6			THF	55:1	20		> 99		5,300	1.08	18
7			THF	179:1	25		> 99		21,030	1.11	18
8			THF	71:1	25		> 99		6,420	1.10	18
9a	 A_3:A_4 = ?:?	none	none	300:1	100	24 h		90	11,400		19
				45:1	15	180 min			5,100	3.1	4
				590:1	170				13,000[(n)]	2.1	20
			toluene	50:1	25	3 h	100		6,500		1
				235:1	25	0.25 h	100		9,000[(n)]	1.20	21
				45:1	110	180 min			2,600	2.4	4
				482:1	0			100	59,000[(n)]	1.1	20
				590:1	100			100	47,500[(n)]	1.35	20
				500:1	RT	1 h	90		41,800[(n)]	1.66	22
			DCM	500:1	RT	18 h	80		49,790[(n)]	1.21	22
			$scCO_2$ (200 bar)	51:1	110	15 min		82	7,650	2.3	4
				40:1	110	1 h		97	8,300	4.0	23
9b			toluene	10:0.1:1	50		100			1.1	24
9c			THF	19.8:0.035:1	25				3,200[(n)]	1.18	25
				8.5:0.015:1	25				2,180[(n)]	1.16	25
			toluene	14050:38:1	25	48 h		97	12,300(n)	1.34	20
				3500:9.5:1	25	48 h		97	6,200(n)	1.12	20
9d			THF	18.9:0.033:1	25				2,250[(n)]	1.16	25

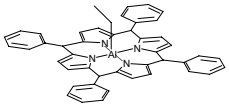
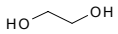
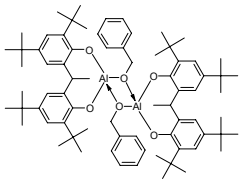
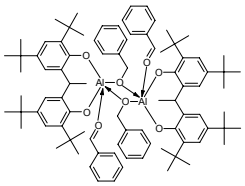
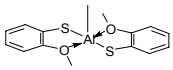
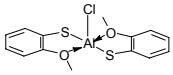
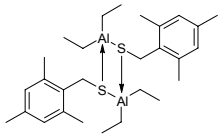
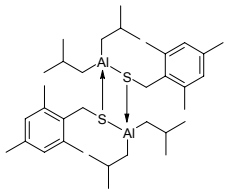
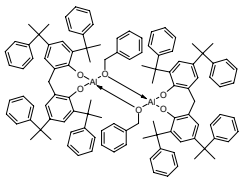
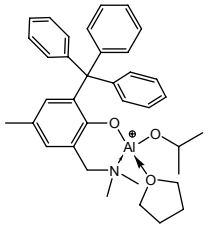
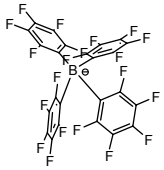
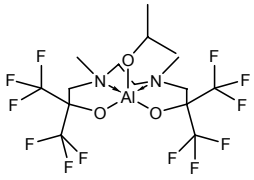
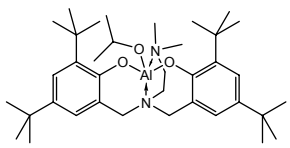
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
9e	A_3:A_4 = 100:0	none	toluene	333:1	20	0.2 h	100		12,200$^{(n)}$	1.10	26
			THF	3000:1	25	1000 min			108,000$^{(n)}$	1.03	27
9f	A_3:A_4 = 95:5	none	THF	571:1	25	<10 min	86				25
9g		HO(CH$_2$)$_4$OH	THF	10:0.0175:1	25	285 min	86				25
9h	A_3:A_4 = 90:10	none	toluene	200:1	0	30 min			29,000$^{(n)}$	1.1	28
9i		none	THF	20:1	25	15 min	86				25
9j		HO(CH$_2$)$_4$OH	THF	10:0.0175:1	25	250 min	84		990$^{(n)}$	1.13	25
				20:0.035:1	25	225 min	86				25
			benzene	9:0.016:1	25	160 min	86				25
9k	A_3:A_4 = 50:50	HO(CH$_2$CH$_2$O)$_{19}$OH	THF	20:0.035:1	25	35 min	86				25
9l			THF	20:0.035:1	25	600 min	86				25
			benzene	9:0.016:1	25	1000 min	81				25
9m			THF	20:0.035:1	25	785 min	80				25
9n	A_3:A_4 = 45:55	none	toluene	200:1	0	30 min			28,000$^{(n)}$	1.1	28
9o	A_3:A_4 = 0:100	none	THF	500:1	25	4000 min			280,000$^{(n)}$		27
				68:1	25	2000 min			49,400$^{(n)}$	1.45	27
9p				571:1	25	300 min	6				25
		HO(CH$_2$)$_4$OH	THF	10:0.0175:1	25	270 min	86				25
10			toluene	17:0.06:1	40	4 h	100		2,100		29
11			toluene	167:1	0				9,500		30
12			toluene	200:1	0				33,500		30
13			toluene	173:1	0				11,200		30
14			toluene	88:1	0				14,100		30
15			toluene	174:1	0				28,500		30
16			toluene	87:1	0				11,750		30
17a			DCM	300:0.3:1	RT	23 h	93		32,100	1.11	15
17b		—OH	DCM	500:0.3:1	RT	42 h	92		62,600	1.14	15

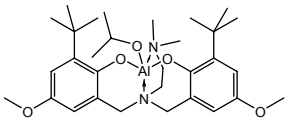
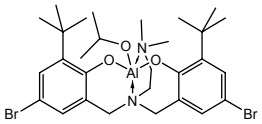
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
18			DCM	50:0.3:1	RT	5 h	95		6,300	1.27	15
19			DCM	50:0.3:1	RT	2 h	100		6,800	1.22	15
20			THF	10:0.25:1	80		≈100		1,290		31
21			DCM	50:1	25	3 h	100		6,600		1
				10:1					3,100	1.40	32
22			toluene	500:0.5:1	25	72 h	100		42,030$^{(n)}$	1.6	33
23			toluene	500:0.5:1	25	72 h	95		36,590$^{(n)}$	1.5	33
24			toluene	500:0.5:1	25	12 h	99		49,500$^{(n)}$	1.7	33
25a		none	toluene	2000:1	25	24 h	46		44,640$^{(n)}$	2.6	33
25b			none	500:0.25:1	80	20 min	71		15,900$^{(n)}$	1.3	33
			toluene	500:0.25:1	25	24 h	98		60,750$^{(n)}$	1.5	33
				500:0.25:1	80	20 min	91		15,400$^{(n)}$	1.1	33
26			toluene	500:1:1	25	11 h	50		26,690$^{(n)}$	1.1	33
27			toluene	500:0.5:1	25	11 h	37		24,480$^{(n)}$	1.2	33
28			toluene	50:1	50	20 h			2,700$^{(n)}$		34
29			toluene	50:1	50						34
30			toluene	50:1	50						34

entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
31			toluene	50:1	50						34
32			toluene	250:1:1	60	60 min		84	43,500$^{(n)}$	1.61	35
33			toluene	250:1:1	60	120 min		41	28,800$^{(n)}$	1.39	35
34			toluene	250:1:1	60	120 min		7.7	9,700$^{(n)}$	1.06	35
35a			toluene	250:1:1	60	30 min		99	56,000$^{(n)}$	1.64	35
				500:1:1	60	45 min		95	100,500$^{(n)}$	1.86	35
35b			toluene	250:1:1	60	30 min		99	72,600$^{(n)}$	1.61	35
36			toluene	200:1:1	70	4.5 min		95.6	23,600$^{(n)}$	1.14	36
				400:1:1	70	14 min		92.6	46,800$^{(n)}$	1.56	36
37			toluene	100:1:1	70	2.5 min		95.6	11,300$^{(n)}$	1.21	36
38			toluene	100:1:1	70	3 min		93.6	11,800$^{(n)}$	1.27	36
39			toluene	100:1:1	70	3.1 min		95.1	10,800$^{(n)}$	1.25	36
40			toluene	100:1:1	70	4.0 min		93.2	11,500$^{(n)}$	1.24	36
41			toluene	100:1:1	70	4.7 min		93.7	12,600$^{(n)}$	1.28	36

entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
42			toluene	100:1:1	25	24 h	31		8,900$^{(n)}$	1.06	[37]
43			toluene	100:1:1	25	24 h	80		19,600$^{(n)}$	1.27	[37]
44			toluene	100:1:1	25	24 h	97		26,600$^{(n)}$	1.19	[37]
45			toluene	100:1:1	25	2 h	92		30,500$^{(n)}$	1.16	[37]
46			toluene	100:1:1	25	1 h	86		26,100$^{(n)}$	1.18	[37]
47			toluene	100:1:1	25	24 h	99		29,600$^{(n)}$	1.22	[37]
48			toluene	100:1:1	25	24 h	31		6,700$^{(n)}$	1.05	[37]
49			toluene	100:1:1	25	24 h	94		25,800$^{(n)}$	1.17	[37]

entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
50			toluene	100:1:1	25	24 h	98		27,400$^{(n)}$	1.14	[37]
51			toluene	100:1:1	25	1 h	94		30,800$^{(n)}$	1.16	[37]
52			toluene	100:1:1	25	10 min	95		29,200$^{(n)}$	1.16	[37]
53			toluene	100:1:1	25	10 min	96		29,800$^{(n)}$	1.16	[37]
				300:1:1	25	60 min	98		77,100$^{(n)}$	1.16	[37]
				300:1:1	70	1 min	91		73,500$^{(n)}$	1.19	[37]
54			toluene	100:1:1	25	10 min	94		29,700$^{(n)}$	1.28	[37]
55			toluene	100:1:1	25	10 min	89		33,100$^{(n)}$	1.26	[37]
56			toluene	100:1:1	25	10 min	47		18,100$^{(n)}$	1.16	[37]
57			toluene	100:1:1	25	10 min	72		27,300$^{(n)}$	1.14	[37]
58a		none	DCM	200:1	RT	4 h	71		23,000	1.49	[38]
58b		—OH	DCM	200:1:9	RT	220 h	100		2,300	1.08	[38]
			none	200:1:4	RT	4 h	65		3,500	1.07	[38]
59		—OH	none	200:1:9	50	13 days	97		2,000	1.12	[38]

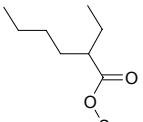
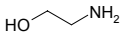
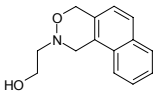
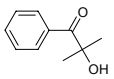
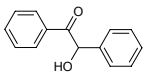
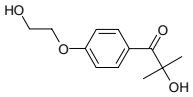
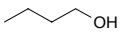
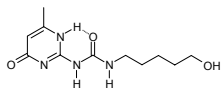
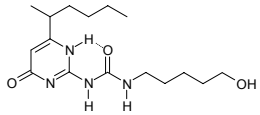
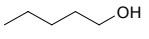
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
60			none	200:1:1	50	21 days	49		10,400	1.18	[38]
				200:1:1	50	24 days	100		2,600	1.12	[38]
61a		none	toluene	200:1	25	48 h		95	43,900	1.15	[39]
61b			toluene	50:0.5:1	25	24 h		95	7,100	1.07	[39]
62		none	toluene	50:1	25	16 h		69	7,900	1.04	[39]
63			toluene	200:1	25	2 h	93	93	45,300	1.19	[40]
64			toluene	200:1	25	2 h	100	99	58,300	1.41	[40]
65			toluene	200:1	25	5 h	100	99	117,200	1.37	[40]
66			toluene	60:1	25	20 h	100	96	26,100	1.21	[40]
67a		none	toluene	400:1	53	5 h	96	94	41,500	1.16	[41]
67b			toluene	200:0.5:1	53	3 h	99	93	27,900	1.04	[41]
68			DCM	120:1	RT	1 h		99	14,157[(n)]	1.53	[42]
				120:1	45	15 min		99	15,330[(n)]	1.38	[42]
69			DCM	1000:1	RT	15 h	98		141,400[(n)]	1.23	[22]
			toluene	500:1	RT	3 h	94		45,400[(n)]	1.58	[22]
70			toluene	500:1	RT	48 h	84		46,300[(n)]	1.14	[22]
				100:1	25		99.7		21,800[(n)]	1.04	[43]

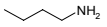
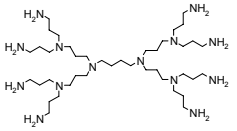
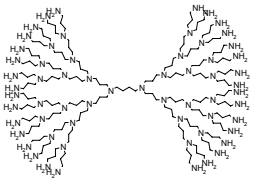
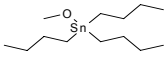
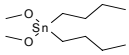
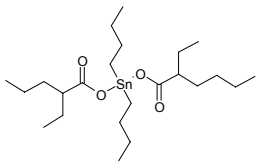
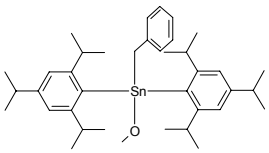
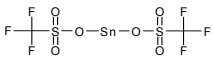
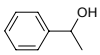
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
71		toluene	100:1	25			Similar than above			43
72		toluene	100:1	25			Similar than above			43

(a) = reaction carried out under air
THF = tetrahydrofuran, $scCO_2$ = supercritical carbon dioxide, DCM = dichloromethane
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
RT = Room Temperature
M = number average molecular weight
(n) = number average molecular weight
PDI = polydispersity index

b. Tin-based catalysts

Table 1.4 – Selected conditions for the ROP of ε-CL using tin-based catalysts, and characteristics of the resulting PCL

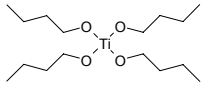
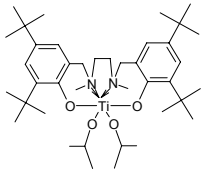
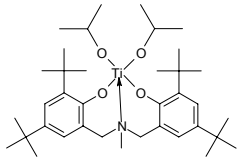
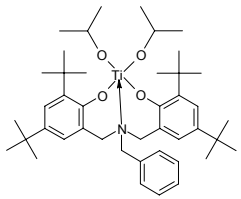
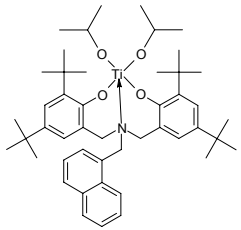
entry	catalyst Initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1a	 None	none	667:1	110				92,000$^{(n)}$	1.77	44
			286:1	130	93 min	98.6		25,300$^{(n)}$	1.57	45
		THF	40:1	80				283,000$^{(n)}$	1.40	46, 47
1b		dioxane	50:1:1	110	42 h	40		2,400$^{(n)}$		1
		toluene	50:1:1	110	21 h	100		5,700$^{(n)}$		1
1c		none	20:0.0025:1	110	48 h		96	7,020$^{(n)}$	1.45	48
			30:0.025:1	110	48 h			9,890$^{(n)}$	1.30	48
1d		none	20:2.5:1	110	5 days		100	1,800$^{(n)}$	1.17	49
1e		none	20:400:1	110	48 h		100	2,600$^{(n)}$	1.08	50
1f		none	20:400:1	110	96 h		100	3,300$^{(n)}$	1.57	50
1g		none	40:200:1	110	90 h		100	4,400$^{(n)}$	1.56	50
1h		none	103:0.5:1	80	3 h	79.1		61,000$^{(n)}$	1.28	51
		THF	6:7:1	80				800$^{(n)}$	1.78	52
			5:10:1	80	6 h	99				53
			167:4:1	80				17,700$^{(n)}$	1.43	46, 47
			103:0.5:1	80	50 h	89.9		70,000$^{(n)}$	1.30	51
		toluene	103:0.5:1	80	46 h	94.9		73,000$^{(n)}$	1.28	51
		$scCO_2$ (240 bar)	103:0.5:1	80	50 h	93.8		68,000$^{(n)}$	1.15	51
1i	H_2O	THF	33:33:1	80				6,000$^{(n)}$		52
1j		THF:$CHCl_3$ (1:1 v/v)	71:1.5:1	80	24 h		73	8,360$^{(n)}$		54
			48:1.5:1	80	24 h		79	19,700$^{(n)}$		54
1k		toluene	15:2:1	80	24 h		95	2,050$^{(n)}$	1.34	54
			69:2:1	80	24 h		92	10,600$^{(n)}$	1.56	54
			179:2:1	80	24 h		94	19,100$^{(n)}$	1.35	54
1l		THF	50:2.5:1	80	24 h		52	5,190$^{(n)}$	1.17	54
			100:2.5:1	80	24 h		67	8,650$^{(n)}$	1.36	54

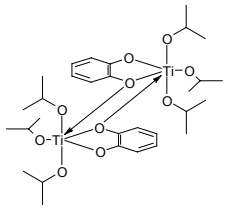
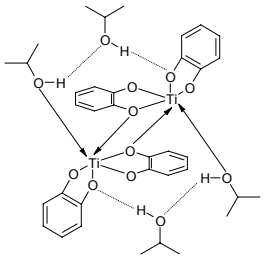
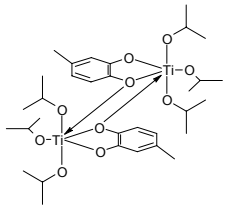
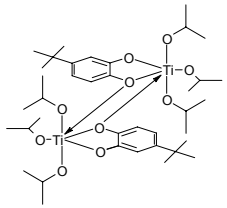
entry	catalyst / Initiator (catalyst/initiator)	solvent	[M]:[C]:[I] ([M]:[C/I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1m		none	30:0.01:1	110	24 h		84	3,500	1.18	55
1n		THF	100:15:1	80						56
1o		THF	858:0.9:1	80				79,000(n)	1.04	56
1p		THF	2607:2.6:1	80				287,500(n)	1.05	56
1q	$Ca_5(PO_4)_3(OH)$	none	339:1.2:1	130	69 min			22,300(n)	1.41	45
2		none	100:1	100	24 h		92	10,273(n)		19
3		none	200:1	100	24 h		92	11,414(n)		19
			360:1	40	20 min	100		21,000(n)	1.80	57
		toluene	362:1	40	3 h	100		21,000(n)	1.60	57
		CFC-113	362:1	40	1 h	58.8		10,700(n)	2.15	57
	$scCO_2$	(200 bar)	131:1	60	60 min		95	14,300(n)	1.6	58
		(210-215 bar)	364:1	40	9.75 h	92.0		18,500(n)	1.85	57
4		none	30:0.01:1	110	24 h		83	3,100	1.12	55
5		toluene	120:1	75	24 h	86.2		19,753(n)	1.4	59
6a		none	30:0.01:1	20	48 h		100	3,420	1.06	55, 60
			150:0.01:1	65	2 h		90	11,400	1.4	60
			30:0.01:1	110	3 h		95	3,800	1.3	55
		toluene	30:0.01:1	20	14 h		90	3,300	1.05	60
			150:0.01:1	65	4 h		85	11,400	1.41	60
6b		none	30:0.01:1	40	18 h		98	3,100	1.08	55
			30:0.01:1	65	6 h		82	2,700	1.10	55
6c		none	30:0.01:1	40	18 h		100	4,000	1.12	55
			30:0.01:1	65	6 h		70	2,900	1.13	55

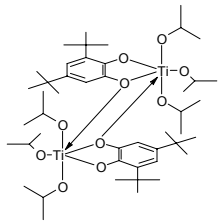
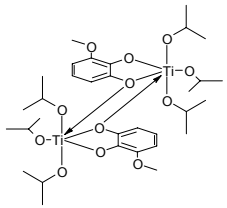
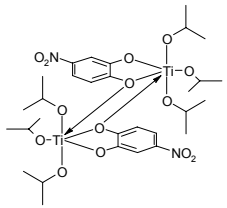
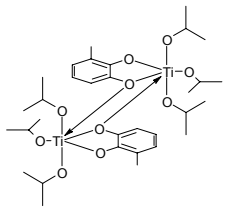
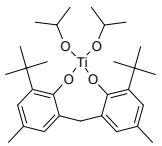
THF = tetrahydrofuran, $scCO_2$ = supercritical carbon dioxide, CFC-113 = 1,1,2-trichloro-1,2,2-trifluoroethane
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst
M = molecular weight
(n) = number average molecular weight
PDI = polydispersity index

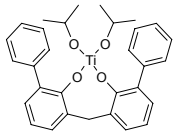
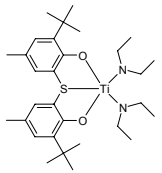
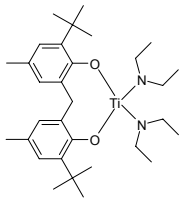
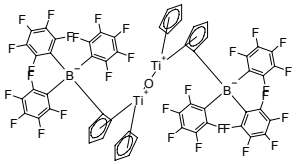
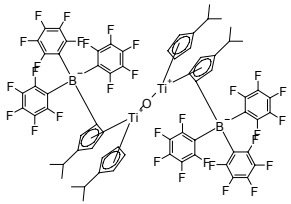
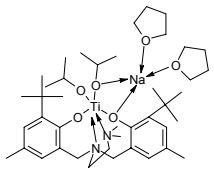
4. Transition metal-based catalysts

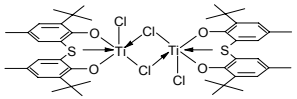
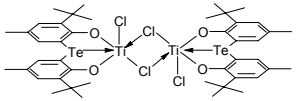
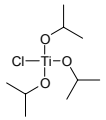
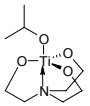
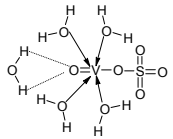
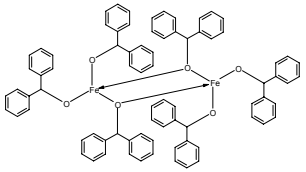
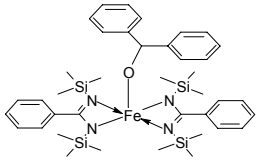
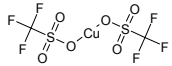
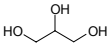
Table 1.5 – Chosen conditions for the ROP of ε-CL using transition metal-based catalysts, and characteristics of the resulting PCL

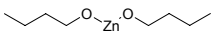
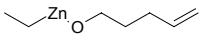
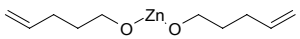
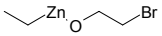
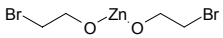
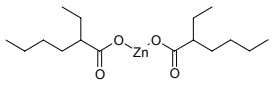
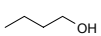
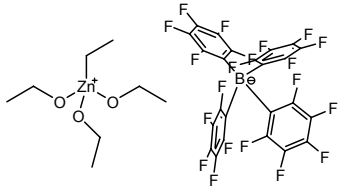
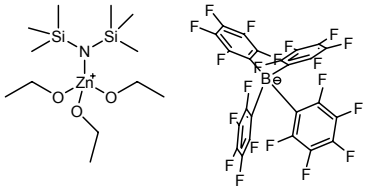
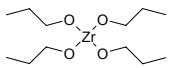
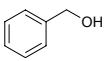
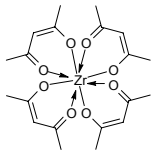
entry	catalyst / initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1		none	400:1	100	24 h		93	$10,843^{(n)}$		19
			4400:1	180	15 min	90		$90,000^{(n)}$		61
		toluene	100:1	100	6 h		low conversion			62
2		toluene	100:1	RT	24 h		> 99	$8,500^{(n)}$	2.60	63
3		toluene	100:1	20	24 h		> 99	$6,700^{(n)}$	1.24	64
4		toluene	100:1	20	24 h		> 99	$7,100^{(n)}$	1.11	64
5		toluene	100:1	20	24 h		> 99	$6,000^{(n)}$	1.08	64

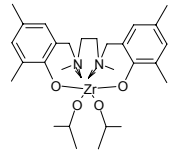
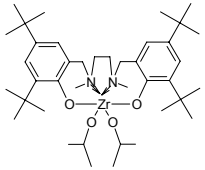
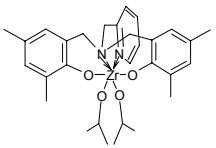
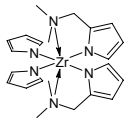
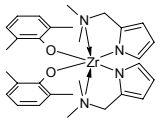
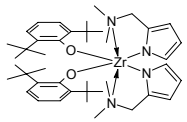
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
6		toluene	100:1	20	24 h		79	2,100$^{(n)}$	1.19	[65]
7		toluene	100:1	20	24 h		25	1,300$^{(n)}$	1.22	[65]
8		toluene	100:1	20	24 h		61	2,600$^{(n)}$	1.20	[65]
9		toluene	100:1	20	24 h		5	1,200$^{(n)}$	1.13	[65]

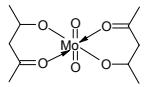
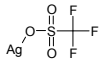
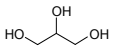
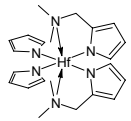
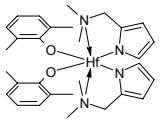
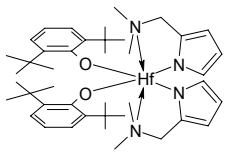
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
10		toluene	100:1	20	24 h		71	3,500$^{(n)}$	1.27	[65]
11		toluene	100:1	20	24 h		4	1,300$^{(n)}$	1.24	[65]
12		toluene	100:1	20	24 h		29	1,500$^{(n)}$	1.18	[65]
13		toluene	100:1	20	24 h		45	2,050$^{(n)}$	1.17	[65]
14		DCM	100:1	25	5 h	100		6,500$^{(n)}$	1.15	[66]

entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
15		DCM	100:1	25	75 h	100		5,600$^{(n)}$	1.10	66
16		toluene	200:1	100	32 h		90.3	18,800$^{(n)}$	1.31	67
17		toluene	200:1	100	8 h		91.0	56,200$^{(n)}$	1.60	67
18		none	6000:1	60	8 days		69	538,000$^{(w)}$		68
		toluene	2500:1	60	10 days		96	265,000$^{(w)}$		68
19		none	1000:1	60	8 days		97	216,000$^{(w)}$		68
20		toluene	200:1	60	2 h	97.4		32,500$^{(w)}$	2.5	8

entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
21		none	100:1	100	6 h		93	62,200$^{(n)}$	2.07	62
		toluene	100:1	100	6 h		100	72,300$^{(n)}$	2.28	62
		anisole	200:1	100	5 h		91	28,200$^{(n)}$	1.17	62
22		none	100:1	100	12 h		55	45,100$^{(n)}$	1.65	62
		toluene	100:1	100	6 h		88	26,000$^{(n)}$	1.20	62
		anisole	200:1	100	8 h		93	12,500$^{(n)}$	1.08	62
		dioxane	200:1	100	8 h		92	20,200$^{(n)}$	1.08	62
23		toluene	175:1	70	24 h	77		15,800$^{(n)}$	1.06	69
24		toluene	200:1	70	24 h	89		17,600$^{(n)}$	1.10	69
25		methanol$^{(O)}$	133:1	60	24 h	99	99			70
		THF:H_2O $^{(O)}$ (7:3 v/v)		60	24 h	99	98			70
26		toluene	450:1	25	16 h	100		36,400$^{(n)}$	1.20	71
27		toluene	400:1	25	16 h	100		27,000$^{(n)}$	1.98	71
28	 	none$^{(a)}$	150:0.3:1	60	24 h		86	16,400$^{(n)}$	1.97	14
29	ZnO	[bmim][BF_4]	143:1	255 $^{(MW)}$			9	2,260$^{(w)}$	1.3	72

entry	catalyst (catalyst/initiator)	initiator	solvent	[M]:[C]:[I] ([M]:[C/I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
				143:1	305 (MW)			62	11,060(w)	2.5	72
30			none	200:1	100	24 h		93	10,843 (n)		19
31			toluene		25			*no reported results*			73
32			toluene		25				3,100(n)	1.05	73
33			toluene	45:1	25		88		4,500(n)	1.09	73
				90:1	25				11,400(n)		73
34			toluene	53:1	25		100		3,200(n)	1.1	73
				260:1	25				15,500(n)		73
35a		none	THF	100:1	80		≈100		440,000(n)	1.04	31
35b			none	30:1:1	100		≈100		3,350(n)	1.98	74
			THF	200:5:1	80		≈100		25,000(n)		31
36			toluene	1000:1	22	120 min		93.5			75
37			none	6000:1	50	20 min		14.5	55,000(w)	2.3	75
38a		none	none	400:1	100	24 h		92	11,756 (n)		19
38b			toluene	10:0.1:1	50		100				24
39			benzene	50:1	80	10 h	95		6,600	1.5	76

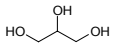
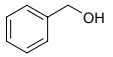
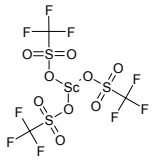
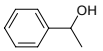
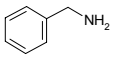
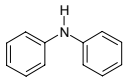
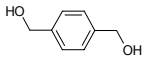
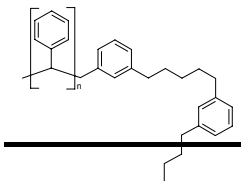
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
40		toluene	100:1	RT	24 h		> 99	6,000$^{(n)}$	2.60	63
41		toluene	100:1	RT	24 h		10	1,000$^{(n)}$	1.59	63
42		toluene	100:1	RT	24 h		> 99	7,500$^{(n)}$	1.27	63
43		toluene	100:1	25			96	18,457$^{(n)}$	2.63	77
44		toluene	100:1	50			76	21,219$^{(n)}$	1.55	77
45		toluene	100:1	50			93	14,764$^{(n)}$	1.38	77
46	aqueous $H_5[PMo_{10}V_2O_{40}]$	methanol$^{(O)}$	133:1	60	12 h	99	98	4,900$^{(w)}$	≤ 1.7	70
		methanol	133:1	60	24 h	30	26			70
		methanol$^{(a)}$	133:1	60	12 h	99	98			70
		THF$^{(O)}$	133:1	60	1 h	99	99			70
		ethanol:H_2O $^{(O)}$ (v/v 9:1)	133:1	60	24 h	90	86			70

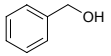
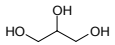
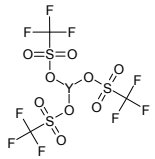
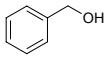
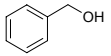
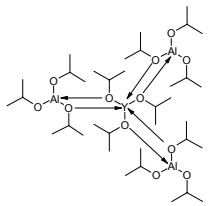
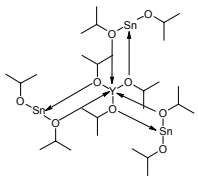
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
		acetonitrile$^{(O)}$	133:1	60	24 h	90	87			70
		toluene	133:1	60	24 h	99	96			70
47	aqueous $H_3[PMo_{12}O_{40}]$	methanol$^{(O)}$	161:1	60	24 h	99	79			70
48	aqueous $H_6[PMo_9V_3O_{40}]$	methanol$^{(O)}$	133:1	60	12 h	99	98			70
49		methanol$^{(O)}$	13:1	60	24 h	99	96			70
50	 	none	150:0.3:1	60	240 h		46	6,700$^{(n)}$	1.89	14
51	aqueous $H_3[PW_{12}O_{40}]$	methanol$^{(O)}$	161:1	60	24 h	98	98			70
52		toluene	100:1	25			99	52,962$^{(n)}$	1.45	77
53		toluene	100:1	50			75	17,727$^{(n)}$	1.38	77
54		toluene	100:1	50			94	10,907$^{(n)}$	1.23	77

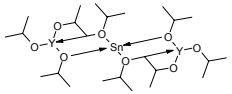
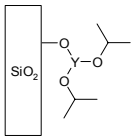
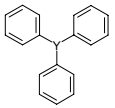
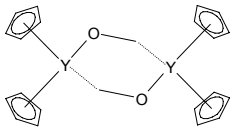
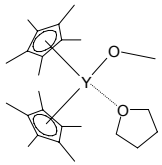
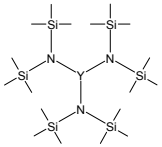
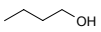
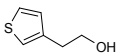
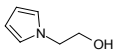
(O) = reaction performed under dioxygen atmosphere, (a) = reaction carried out under air
DCM = dichloromethane, THF = tetrahydrofuran
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator
RT = Room Temperature
(MW) = microwave heating
M = molecular weight
(n) = number average molecular weight, (w) = weight average molecular weight
PDI = polydispersity index

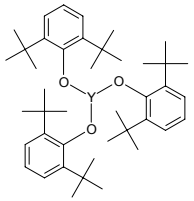
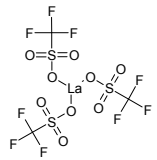
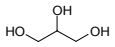
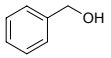
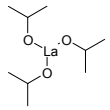
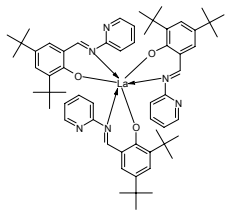
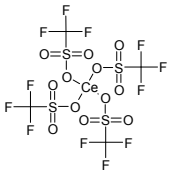
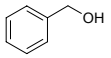
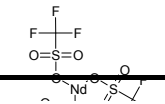
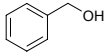
5. Rare earth metal-based catalysts

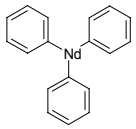
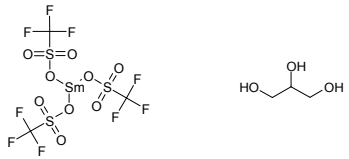
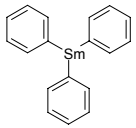
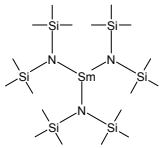
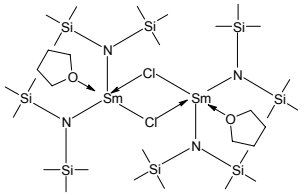
Table 1.6 – Chosen conditions for the ROP of ε-CL using rare earth metal-based catalysts, and characteristics of the resulting PCL

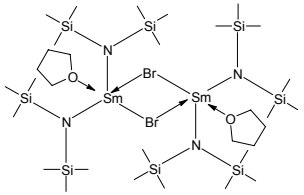
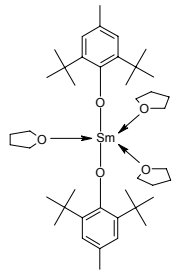
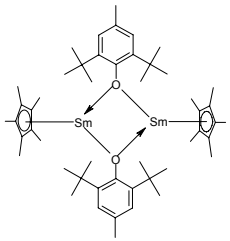
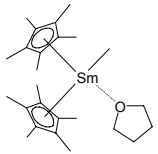
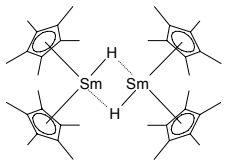
Entry	catalyst (catalyst/initiator)	initiator	Solvent	[M]:[C]:[I] ([M]:[C/I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
1a		none	Toluene	50:1	25	4 h		> 99	6,900$^{(n)}$	1.13	78
			[BMIM][PF_6]	50:1	25	42 h		80	2,500$^{(n)}$	1.44	79
			[BMIM][SbF_6]	50:1	25	30 h		87	900$^{(n)}$	1.31	79
1b			none[(a)]	150:0.3:1	60	6 h		66	11,400$^{(n)}$	1.66	14
1c		H_2O	Toluene	50:0.05:1	25	120 h		> 99	7,700$^{(n)}$	1.10	78, 79
1d			Toluene	50:0.05:1	25	120 h		> 99	7,500$^{(n)}$	1.12	78
				50:1:1	25	2.3 h		> 99	3,500$^{(n)}$	1.13	78, 79
1e			None	30:0.01:1	40	24 h	81		3,000	1.08	55
				30:0.01:1	110	3 h	89		5,200	1.12	55
			Toluene	40:0.4:1	35	21 h	98		6,100$^{(n)}$	1.16	80
1f			None	30:0.01:1	40	24 h	85		3,300	1.08	55
				30:0.01:1	65	8 h	64		1,900	1.33	55
1g			None	30:0.01:1	40	24 h	83		2,900	1.07	55
				30:0.01:1	65	8 h	64		2,300	1.32	55
1h			Toluene	50:1:1	25	5 days			800$^{(n)}$	1.18	79
1i			Toluene	50:1:1	25	21 h			1,500$^{(n)}$	1.18	79
1j			Toluene	100:2:1	25	3.5 h			11,600$^{(n)}$ + 3,800$^{(n)}$		79
2a			Toluene	40:0.4:1	35	72 h	86		6,200$^{(n)}$	1.12	80
2b			Toluene	40:0.4:1	50	30 h	89		4,700$^{(n)}$	1.13	80

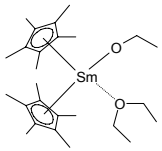
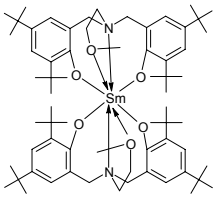
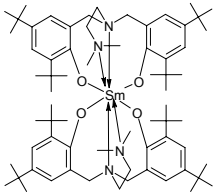
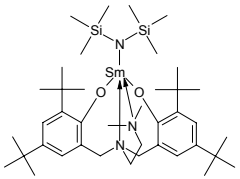
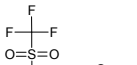
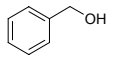
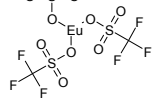
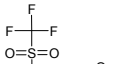
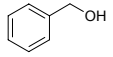
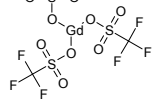
Entry	catalyst / initiator *(catalyst/initiator)*	Solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
2c		Toluene	40:0.4:1	50	18 h	91		4,100$^{(n)}$	1.11	80
2d	H_2O	Toluene	40:0.4:1	50	8 h	81		2,800$^{(n)}$	1.26	80
3a		none[(a)]	150:0.03:1	60	48 h		54	13,300$^{(n)}$	1.45	14
3b	 	Toluene	50:1:1	25	120 h		100	1,700$^{(n)}$	1.29	79
3c		[BMIM][BF_4]	50:1	25	7 days		29	500$^{(n)}$	1.15	79
	none	[BMIM][PF_6]	50:1	25	53 h		83	2,800$^{(n)}$	1.42	79
		[BMIM][SbF_6]	50:1	25	48 h		99	1,800$^{(n)}$	1.24	79
4a	 none	None	47:1	110	15 min			5,180$^{(n)}$	8.0	4
		Toluene	500:1	5	30 min		97	45,900$^{(n)}$		81
			146:1	110	15 min			7,800$^{(n)}$	1.8	4
		$scCO_2$ (150 bar)	58:1	106	15 min		95	15,400$^{(n)}$	1.8	4
		$scCO_2$ (200 bar)	40:1	110	1 h		76	6,000$^{(n)}$	1.4	23
4b		Toluene	13:0.1:1	50	5 min			1,950$^{(n)}$	1.55	24
5		Toluene	1250:1	10	50 min		97	13,300$^{(n)}$		81
6		Toluene	1000:1	40	5 min		97	12,600$^{(n)}$		81

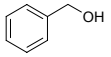
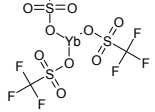
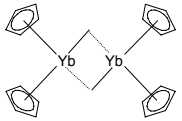
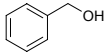
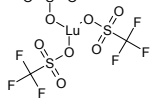
Entry	catalyst initiator *(catalyst/initiator)*	Solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
7		Toluene	1000:1	10	5 min		97	54,000[(n)]		81
8	 	Toluene	22:0.1:1[(b)]	20	2.4 h	100		1,900[(n)]	1.3	29
			20:0.07:1[(b)]	40	2.5 h	100		1,300[(n)]	1.5	29
			22:0.1:1[(c)]	40	9 min	100		1,900[(n)]	1.1	29
		THF	22:0.1:1[(c)]	40	60 min	100		2,000[(n)]	1.1	29
9		None	250:1	60	30		81	88,000[(n)]		2
			250:1	100	30		91	89,000[(n)]		2
10		Toluene	500:1	0	10 h	95		92,000[(n)]	1.10	82
11		Toluene	500:1	0	10 h	90		89,000[(n)]	1.12	82
12a		none	Toluene	13:1	25			8,000[(n)]	3.1	83
12b			Toluene	175:10:1	40	3 min	100	22,000[(n)]	1.1	83
12c			Toluene	44:8:1	20	3.5 min	99	4,800[(n)]	1.2	83
12d			Toluene	22:7:1	20	1.5 min	100	2,500[(n)]	1.2	83
12e			Toluene	43:10:1	20	3 min	100	4,500[(n)]	1.3	83
12f			Toluene	26:7:1	20	3.5 min	100	3,400[(n)]	1.15	83
12g			Toluene	26:8:1	20	3.5 min	100	3,600[(n)]	1.15	83

Entry	catalyst (catalyst/initiator)	initiator	Solvent	[M]:[C]:[I] ([M]:[C/I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
13			DCM	50:0.3:1	22	5 min	100		6,000$^{(n)}$	1.14	84
14a			none$^{(a)}$	150:0.3:1	60	240 h			300$^{(n)}$	2.90	14
14b			Toluene	50:1:1	25	3 h		100	2,900$^{(n)}$	1.16	79
14c		none	[BMIM][BF_4]	50:1	25	2 days		29	300$^{(n)}$	1.16	79
			[BMIM][PF_6]	50:1	25	46 h		100	3,700$^{(n)}$	1.53	79
			[BMIM][SbF_6]	50:1	25	42 h		100	1,800$^{(n)}$	1.21	79
15			None	32:1	110	15 min			7,300$^{(n)}$	6.2	4
			Toluene	140:1	110	7 min		80	16,500$^{(n)}$	1.5	4
			$scCO_2$ (150 bar)	140:1	110	15 min		25	5,050$^{(n)}$	1.4	4
			$scCO_2$ (200 bar)	40:1	110	1 h		46	3,100$^{(n)}$	1.2	23
16			Toluene	2000:1	0	2 h	60		14,400$^{(v)}$		85
				2000:1	30	2 h	75		38,900$^{(v)}$		85
				2000:1	50	2 h	91		44,300$^{(v)}$		85
				2000:1	60	2 h	94		45,700$^{(v)}$		85
				2000:1	80	2 h	100		48,300$^{(v)}$		85
17a			Toluene	50:1:1	25	8.5 h		100	1,800$^{(n)}$	1.21	79
17b		none	[BMIM][BF_4]	50:1	25	6 days		32	600$^{(n)}$	1.20	79
			[BMIM][PF_6]	50:1	25	47 h		100	3,500$^{(n)}$	1.56	79
			[BMIM][SbF_6]	50:1	25	29 h		100	1,700$^{(n)}$	1.22	79
18a			Toluene	50:1:1	25	120 h		70	900$^{(n)}$	1.19	79
18b		none	[BMIM][BF_4]	50:1	25	6 days		30	300$^{(n)}$	1.20	79

Entry	catalyst initiator *(catalyst/initiator)*	Solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
		[BMIM][PF_6]	50:1	25	35 h		100	2,700$^{(n)}$	1.41	79
		[BMIM][SbF_6]	50:1	25	43 h		100	1,700$^{(n)}$	1.27	79
19		None	500:1	80	30 min		96	14,600		2
20		Toluene	13:0.1:1	50	10 min	100		1,550$^{(n)}$	1.1	24
21		none[(a)]	50:0.3	60	240 h			300$^{(n)}$	3.50	14
22		None	1000:1	170	5 min		87	17,800$^{(n)}$		2
		Toluene	125:1	70	2 h		65	68,000$^{(n)}$		2
		Benzene	125:1	70	2 h		70	53,000$^{(n)}$		2
23		Toluene	13:0.1:1	50	5 min	100		1,100$^{(n)}$	1.9	24
24		Toluene	150:1	20	< 1 min		98	27,200$^{(n)}$	2.38	86
25		Toluene	150:1	20	20 min		98	11,000$^{(n)}$	1.91	86
			300:1	20			98	13,300$^{(n)}$	1.57	86

Entry	catalyst initiator *(catalyst/initiator)*	Solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
26		Toluene	75:1	20			97	16,600	1.65	[86]
			150:1	20	10 min		98	17,500	1.65	[86]
			150:1	-10			98	31,000	1.98	[86]
27		Toluene	500:1	RT	2 min	100		153,000$^{(n)}$	1.43	[87]
			2000:1	RT	5 min	100		626,000$^{(n)}$	1.56	[87]
28		Toluene	500:1	RT	2 min	99		123,000$^{(n)}$	1.40	[87]
29		Toluene	500:1	25	5 h	95		83,400$^{(n)}$	1.06	[82]
30		Toluene	500:1	20	5 h	65		142,200$^{(n)}$	1.05	[82]

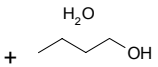
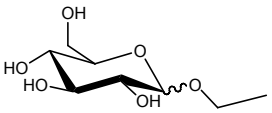
Entry	catalyst initiator *(catalyst/initiator)*	Solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
31		Toluene	500:1	0	10 h	92		108,000$^{(n)}$	1.09	82
32		THF	275:1	RT	2 min	71		91,575$^{(n)}$	2.7	88
33		THF	275:1	RT	2 min	71		51,750$^{(n)}$	3.3	88
34		THF	275:1	RT	2 min	67		30,060$^{(n)}$	2.0	88
35a	 	Toluene	50:1:1	25	114 h		100	1,700$^{(n)}$	1.22	79
35b	 none	[BMIM][PF_6]	50:1	25	49 h		100	2,400$^{(n)}$	1.45	79
		[BMIM][SbF_6]	50:1	25	48 h		44	1,500$^{(n)}$	1.13	79
36a	 	Toluene	50:1:1	25	120 h		74	1,600$^{(n)}$	1.17	79
36b	 none	[BMIM][BF_4]	50:1	25	5 days		30	600$^{(n)}$	1.21	79
		[BMIM][PF_6]	50:1	25	48 h		100	3,400$^{(n)}$	1.50	79
		[BMIM][SbF_6]	50:1	25	29 h		100	2,500$^{(n)}$	1.25	79

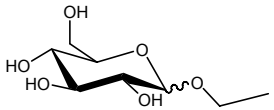
Entry	catalyst *(catalyst/initiator)*	initiator	Solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
37a			Toluene	50:1:1	25	30 h		100	1,700$^{(n)}$	1.23	[79]
37b		none	[BMIM][BF_4]	50:1	25	4 days		27	500$^{(n)}$	1.21	[79]
			[BMIM][PF_6]	50:1	25	48 h		43	1,600$^{(n)}$	1.53	[79]
			[BMIM][SbF_6]	50:1	25	48 h		82	1,400$^{(n)}$	1.21	[79]
38			Toluene	500:1	20	5 h	25		56,600$^{(n)}$	1.19	[82]
39a			Toluene	50:1:1	25	91 h		99	2,200$^{(n)}$	1.30	[79]
39b		none	[BMIM][BF_4]	50:1	25	3 days		26	500$^{(n)}$	1.17	[79]
			[BMIM][PF_6]	50:1	25	47 h		100	4,400$^{(n)}$	1.49	[79]
			[BMIM][SbF_6]	50:1	25	48 h		80	1,100$^{(n)}$	1.18	[79]

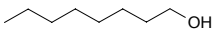
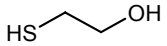
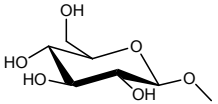
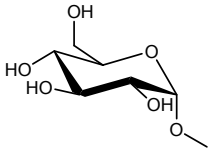
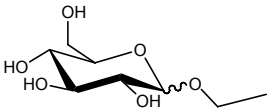
(a) = reaction carried out under air
BMIM = 1-butyl-3-methylimidazolium, THF = tetrahydrofuran, DCM = dichloromethane, $scCO_2$ = supercritical carbon dioxide
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator
(b) polymer recovered by HCl hydrolysis + decantation ; (c) polymer recovered by MeOH hydrolysis + decantation
RT = Room Temperature
M = molecular weight
(n) = number average molecular weight, (v) = viscosimetric average molecular weight
PDI = polydispersity index

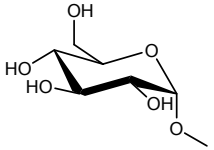
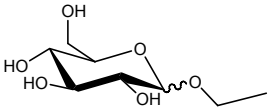
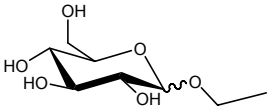
Enzymatic Ring-Opening Polymerisation (eROP)

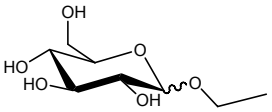
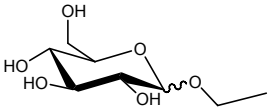
Table 1.7 – Selected conditions for the eROP of ε-CL and characteristics of the resulting PCL

entry	catalyst	initiator(s)	solvent	$m_M:m_C(:m_I)$	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1a	crude PPL	H_2O	none	87:65:1	65	4 days			$1,100^{(n)}$	1.4	89
			heptane	96:143:1	65	4 days	100		$2,700^{(n)}$	1.9	89
1b		H_2O + 	dioxane	18.3:27.3:(0.19+0.81)	65	4 days			$310^{(n)}$		89
			toluene	18.3:27.3:(0.19+0.81)	65	4 days			$750^{(n)}$		89
			heptane	18.3:27.3:(0.19+0.81)	65	4 days	100		$1,600^{(n)}$	1.8	89
				66:99:(0.69+0.31)	65	4 days	100		$2,300^{(n)}$	1.9	89
1c		—OH	none	0.07:94:1	RT	1100 h		45	$2,902^{(w)}$		90
			n-hexane	3.6:4688:1	RT	1100 h		81	$1,364^{(w)}$		90
1d		none	none	2.3:1	60	240 h	95		$1,300^{(n)}$	1.7	91-93
				2.3:1	75	20 days	99		$2,300^{(n)}$	3.1	93
				2.3:1	60	10 days	69		$2,500^{(n)}$	1.9	94
			isooctane	1.1:1	45	10 days	47		$920^{(n)}$	1.6	93
			toluene	1000:1	25-75	500 h					95
1e			none	4.1:2.5:1	70	96 h	> 80	44	$2,200^{(n)}$	1.2	96
				0.02:2.5:1	70			88	$12,500^{(n)}$		96
2	Lipase from *Aspergillus niger* (lipase A)	none	none	2.3:1	60	240 h	4		$780^{(n)}$	1.3	92, 93
3	Lipase from *Candida cylindracea* (lipase B)	none	none	2.3:1	60	10 days	75		$3,300^{(n)}$	2.5	94
				2.3:1	75	10 days	98		$1,800^{(n)}$	2.3	97
4a	Lipase from *Candida cylindracea* (lipase CC)	none	none	2.3:1	60	240 h	92		$1,900^{(n)}$	2.0	91-93
				2.3:1	75	20 days	100		$3,100^{(n)}$	3.0	93
				2.3:1	75	120 h	81		$1,400^{(n)}$	1.7	98
			isooctane	1.1:1	45	20 days	100		$3,700^{(n)}$	2.4	93
			1,4-dioxane	1.1:1	45	10 days	2		$740^{(n)}$	1.1	93
			acetonitrile	1.1:1	45	10 days	1		$690^{(n)}$	1.1	93

entry	catalyst	initiator(s)	solvent	m_M:m_C(:m_I)	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
			acetone	1.1:1	45	10 days	8		$810^{(n)}$	1.1	93
			2-butanone	1.1:1	45	10 days	1		$900^{(n)}$	1.1	93
			tert-butyl alcohol	1.1:1	45	10 days	6		$630^{(n)}$	1.1	93
			tert-butyl methyl ether	1.1:1	45	10 days	37		$500^{(n)}$	1.1	93
			isopropyl ether	1.1:1	45	10 days	48		$710^{(n)}$	1.2	93
			benzene	1.1:1	45	10 days	37		$720^{(n)}$	1.3	93
			carbon tetrachloride	1.1:1	45	20 days	80		$1,000^{(n)}$	2.3	93
			heptane	1.1:1	45	10 days	97		$3,200^{(n)}$	2.7	93
			cyclooctane	1.1:1	45	10 days	100		$1,700^{(n)}$	4.0	93
4b			none	4.1:2.5:1	70	96 h	2				96
5a	lipase from *Candida cylindracea* (= *Candida rugosa*) (*lipase AY*)	H_2O	$^{i}Pr_2O$	0.69:0.2:1	65	5 h	75				99
5b		none	toluene	1000:1	25-75	500 h					95
6	lipase from *Candida cylindracea* (= *Candida rugosa*) (*lipase AY*) supported on poly(propylene)	H_2O	$^{i}Pr_2O$	0.69:0.8:1	65	5 h	85-92				99
7a	lipase from *Candida Antarctica* immobilized on acrylic resin (*Novozym® 435*)	none	none	11.4:1	60	24 h	99		$4,300^{(n)}$	2.7	100
				11.4:1	60	24 h	99		$3,400^{(n)}$	2.5	93
				5.7:1	60	4 h	98		$5,000^{(n)}$	2.5	100
				50:1	60	24 h	98	96	$4,701^{(w)}$		101
				100:1	70	4 h	41		$10,800^{(n)}$	2.1	102
			acetonitrile	5:1	60	48 h	92	37	$1,907^{(w)}$	1.2-1.3	101
				100:1	70	4 h	< 2				102
			THF	5:1	60	48 h	84	18	$1,932^{(w)}$	1.2-1.3	101
				100:1	70	4 h	~ 26				102
			dioxane	5:1	60	48 h	99	29	$2,870^{(w)}$	1.2-1.3	101
				100:1	70	4 h	~ 17				102
			isooctane	5:1	60	24 h	97	94	$3,957^{(w)}$	1.2-1.3	101
				100:1	70	4 h	~ 80		~ $15,000^{(n)}$		102

entry	catalyst	initiator(s)	solvent	$m_M:m_C(:m_I)$	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
			chloroform	100:1	70	4 h	~ 26				102
			butyl ether	100:1	70	4 h	~ 64		~12,500$^{(n)}$		102
			isopropyl ether	100:1	70	4 h	~ 72				102
				100:1	70	4 h	85		17,200$^{(n)}$	1.8	102
			toluene	10:1	70	4 h	87		44,800$^{(n)}$	1.7	102
				1000:1	25-75	500 h					95
			$scCO_2$ (80 bar)	10:1	35	24 h	95		35,000$^{(n)}$	1.4	103
			none	57:1:??*	60	24 h		70	6,740$^{(n)}$	2.73	104
			$^{i}Pr_2O$	0.69:0.03:1	65	5 h	97				99
7b		H_2O	MTBE	23:1:??*	60	72 h		90	2070$^{(n)}$	1.82	104
				1667:167:1	108	5 h	> 93		18,000$^{(n)}$		105
			toluene	526:53:1	60		80		7,000$^{(n)}$		105
				1667:167:1	60		80		15,000$^{(n)}$		105
7c			none	4.4:0.4:1	60	1 h	78		1,000$^{(n)}$	1.5	100
7d			none	57:1.3:1	60	24 h		70	2,940$^{(n)}$	1.42	104
7e			none	17:0.17:1	60	8 h	93	90	3,101$^{(w)}$		106
			acetonitrile	17:3.4:1	60	56 h	95	38	2,141$^{(w)}$	1.3	106
7f			acetonitrile	17:3.4:1	60	56 h	95	37	1,037$^{(w)}$		106
7g			none	4.1:2.5:1	70	96 h	> 80				96
8	Lipase from *Pseudomonas aeroginosa* (lipase PA)	none	none	2.3:1	60	240h	56		2,700$^{(n)}$	3.8	92
9a	Lipase from	—OH	none	3.6:4688:1	60	240 h		56	1,442$^{(w)}$		90
9b	*Pseudomonas cepacia*	none	none	2.3:1	60	240 h		84	6,100$^{(n)}$	2.7	91-93

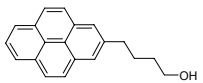
entry	catalyst	initiator(s)	solvent	m_M:m_C(:m_I)	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
9c	(lipase PS-30)		acetonitrile	17:3.4:1	60	100 h	20	20	2,363$^{(w)}$		106
9d			none	4.1:2.5:1	70	96 h	9				96
10	lipase from *Pseudomonas fluorescens* (lipase P)	none	none	2.3:1	75	10 days	92		7,700$^{(n)}$	2.4	94, 97
11	lipase from *Pseudomonas fluorescens* (lipase PF)	none	none	2.3:1	60	10 days	71		7,000(n)	2.2	93
				2.3:1	75	480 h	99		12,000$^{(n)}$	2.3	91-93
				2.3:1	75	120 h	48		4,400$^{(n)}$	2.6	98
			isooctane	1.1:1	45	10 days	52		1,800$^{(n)}$	2.3	93
		H_2O	$^{i}Pr_2O$	0.69:0.2:1	65	5 h	90				99
12	lipase from *Pseudomonas fluorescens* (lipase AK)		none	4.1:2.5:1	70	96 h	54				96
13a		none	none	0.29:1	45	20 days	100		8,800$^{(n)}$	2.58	107
				0.29:1	45				10,187$^{(n)}$	1.28	108
13b	Lipase from *Pseudomonas sp.* (PSL)	H_2O		0.57:1	60	480 h	98		10,200$^{(n)}$	1.45	109
			none	26:1.3:1	45		70		2,700$^{(n)}$	1.70	109
			THF	38:1.9:1	37		28		2,500$^{(n)}$	1.05	109
			1,2-dichloroethane	50:2.5:1	37		45		3,400$^{(n)}$	1.23	109
			chloroform	100:5:1	37		38		2,000$^{(n)}$	1.08	109
			$^{i}Pr_2O$	42:2.1:1	37		99		6,400$^{(n)}$	1.28	109
			benzene	100:5:1	37		58		2,600$^{(n)}$	1.09	109
			toluene	143:7.1:1	37		85		6,500$^{(n)}$	1.35	109
			cyclohexane	250:12.5:1	37		69		7,400$^{(n)}$	1.34	109
			isooctane	143:7.1:1	37		88		7,100$^{(n)}$	1.29	109
14	Lipase from	none	none	2.3:1	60	10 days	38		1,000$^{(n)}$	1.6	93

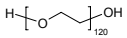
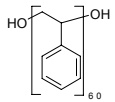
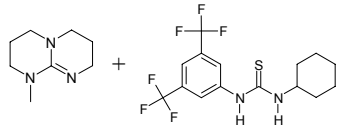
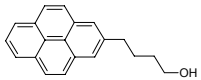
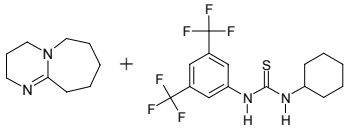
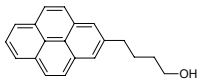
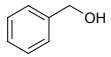
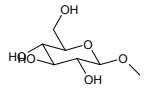
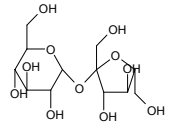
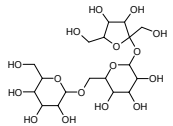
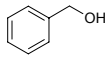
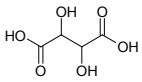
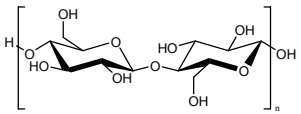
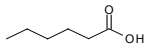
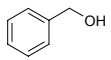
entry	catalyst	initiator(s)	solvent	$m_M:m_C(:m_I)$	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
	Rhyzopus delemer (lipase RD)		isooctane	1.1:1	45	10 days	3		$740^{(n)}$	1.1	93
15	Lipase from *Rhyzopus japonicus* (lipase RJ)	none	none	2.3:1	60	240 h	83		$840^{(n)}$	1.7	91, 93
			isooctane	1.1:1	45	10 days	2		$800^{(n)}$	1.6	93
16	lipase from *Rhizopus miehei (NS-40008)*	H_2O	$^{i}Pr_2O$	0.69:0.03:1	65	5 h	45				99
17	immobilised lipase from *Mucor miehei (Lipozyme® IM)*		none	4.1:2.5:1	70	96 h	15				96
18	Lipase from *Mucor javanicus* (lipase MAP-10)		none	4.1:2.5:1	70	96 h	29				96
19	HLE	none	none	2.3:1	60	10 days	17		$830^{(n)}$	1.2	93
20	Lipolase®	none	toluene	1000:1	25-75	500 h					95

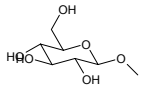
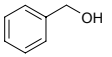
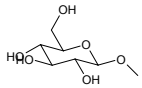
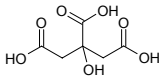
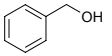
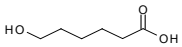
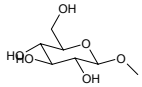
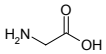
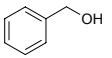
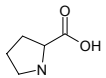
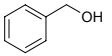
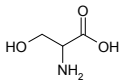
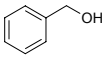
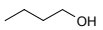
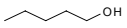
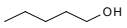
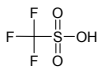
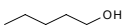
PPL = Porcine Pancreatic Lipase; HLE = Hog Liver Esterase
$scCO_2$ = supercritical carbon dioxide; MTBE = methyl *tert*-butyl ether
m_M = mass of monomer (ε-CL); m_C = mass of catalyst; m_I = mass of initiator
RT = Room Temperature
M = molecular weight
(n) = number average molecular weight, (w) = weight average molecular weight
PDI = polydispersity index

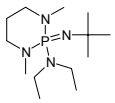
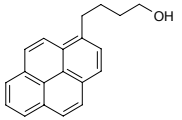
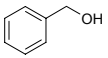
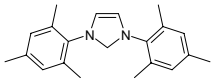
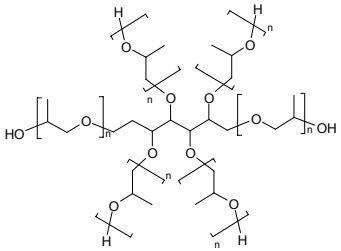
ROP catalysed by organic compounds and inorganic acids

Table 1.8 - Selected conditions for the ROP of ε-CL catalysed by organic compounds and characteristics of the resulting PCL

entry	catalyst	initiator(s)	Solvent	[M]:[C](:[I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1a			benzene-*d6*	50:0.25:1	RT	5 h	76		$8{,}200^{(n)}$	1.10	110, 111
				200:0.25:1	RT	8 h	52		$20{,}800^{(n)}$	1.16	110, 111

entry	catalyst	initiator(s)	Solvent	[M]:[C](:[I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1b			Toluene	50: 0.25 :1	RT	3 h	50		11,100$^{(n)}$	1.03	110, 111
1c			Toluene	150: 0.25 :1	RT	3 h	60		23,400$^{(n)}$	1.11	110, 111
2			benzene-*d6*	20:(0.2+0.2):1	RT	72 h	78		7,700$^{(n)}$	1.05	110
3			benzene-*d6*	20:(0.2+0.2):1	RT	120 h	78		8,100$^{(n)}$	1.04	110
4a			None	30:3:1	120	4 h	78		1,590$^{(w)}$	1.3	112
4b			None	40:1:1	120	21 h	100		6,500$^{(n)}$	1.5	113
4c			None	10:1:1	120	5 h	100		4,000$^{(n)}$	1.5	113
4d			None	10:1:1	120	3 h	100		1,500$^{(n)}$	1.15	113
5a			None	30:3:1	120	4 h	90		2,730$^{(w)}$	1.3	112
5b		 cotton wool	None	100:1:?	120	6 h			not measurable		114
5c		filter paper (Whatman 1)	None	100:1:?	120	6 h			not measurable weight gain: 11%		114
6a			None	30:3:1	120	2 h	10		450$^{(w)}$		112

entry	catalyst	initiator(s)	Solvent	[M]:[C](:[I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
6b			None	10:1:1	120	3 h	20				113
7a			None	30:3:1	120	2 h	12		450$^{(w)}$		112
7b			None	10:1:1	120	3 h	15				113
8			None	30:3:1	120	4 h	81		2,502$^{(w)}$	1.3	112
9			None	10:1:1	120	3 h	30				113
10			None	30:3:1	120	4 h	< 10		450$^{(w)}$		112
11			None	30:3:1	120	4 h	49		1,248$^{(w)}$	1.2	112
12			None	30:3:1	120	4 h	< 5				112
13a	HCl		DCM	100:5:1	25	24 h	94	82	14,300$^{(n)}$	1.15	115
13b			DCM	40:1:1	30	24 h	22		1,610$^{(n)}$	1.19	116
			Toluene	40:1:1	30	19 h	> 98		3,500$^{(n)}$	1.22	116
14a			DCM	40:1:1	30	7 h	> 98		3,500$^{(n)}$	1.22	116
			Toluene	40:1:1	30	1.5 h	> 98		4,500$^{(n)}$	1.15	116
				98:1:1	30	420 min	> 98		10,080$^{(n)}$	1.17	116
14b			Toluene	40:1:1	30	90 min	> 98		4,500$^{(n)}$	1.15	116
			DCM	29:0.4:1	35	90 min	> 95		3,500$^{(n)}$	1.05	117
14c			Toluene	40:1:1	30	110 min	> 98		5,400$^{(n)}$	1.13	116
15a			DCM	40:1:1	30	2 h	> 98		4,280$^{(n)}$	1.07	116
			Toluene	40:1:1	30	1.5 h	> 98		4,300$^{(n)}$	1.07	116
				100:1:1	30	255 min	> 98		9,700$^{(n)}$	1.07	116

entry	catalyst	initiator(s)	Solvent	[M]:[C](:[I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
15b			Toluene	39:1:1	30	90 min	> 98		4,090$^{(n)}$	1.10	[116]
15c			Toluene	40:1:1	30	90 min	> 98		5,100$^{(n)}$	1.08	[116]
16			methanol$^{(O)}$	53:1	60	12 h	99	98			[70]
			THF$^{(O)}$	3:1	60	9 h	99	99			[70]
17			methanol$^{(O)}$	80:1	60	12 h	99	98			[70]
			THF$^{(O)}$	3:1	60	8 h	99	99			[70]
18			None	100:1:1	80	240	14		3,600$^{(n)}$	1.08	[118]
19a			THF	100:0.5:1	25	24 h	99		11,100	1.33	[119]
19b			THF	240:0.5:1	25	24 h	95		4,000	1.15	[119]

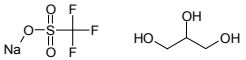
(O) = reaction performed under dioxygen atmosphere
DCM = dichloromethane, THF = tetrahydrofuran
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator
RT = Room Temperature
M = molecular weight
(n) = number average molecular weight, (w) = weight average molecular weight
PDI = polydispersity index

Section 2: Ineffective systems

ROP catalysed by metal-based compounds

1. Alkali-based catalysts

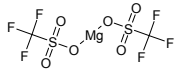
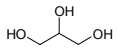
Table 2.1 - Conditions for the ROP of ε-CL using alkali-based catalysts that lead to no polymerisation, low conversion or oligomers

entry	Catalyst Initiator *catalyst/initiator*	solvent	[M]:[C]:[I] [M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1		none[(a)]	150:0.3:1	60	240	no polymerisation				14
2		THF	250:1	20	1 h	oligomers				3

(a) = reaction done under normal atmosphere
THF = tetrahydrofuran
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
M = molecular weight
PDI = polydispersity index

2. Alkaline earth-based catalysts

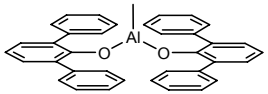
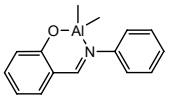
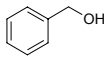
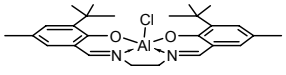
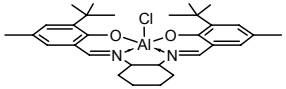
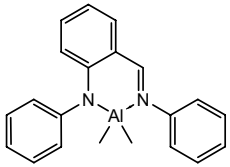
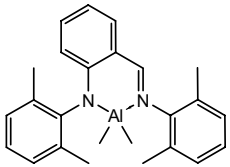
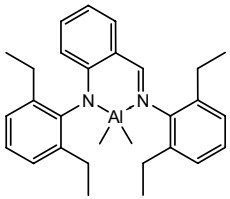
Table 2.2 - Conditions for the ROP of ε-CL using alkaline earth-based catalysts that lead to no polymerisation, low conversion or oligomers

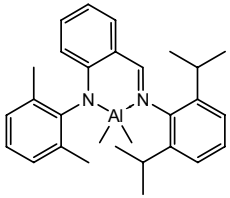
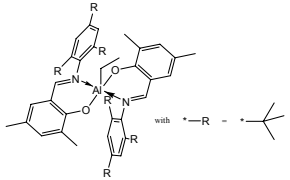
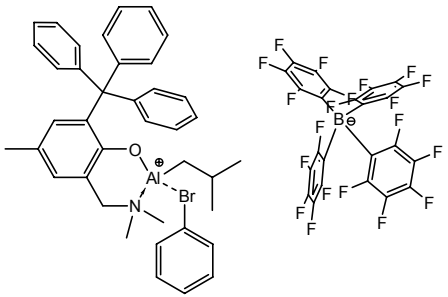
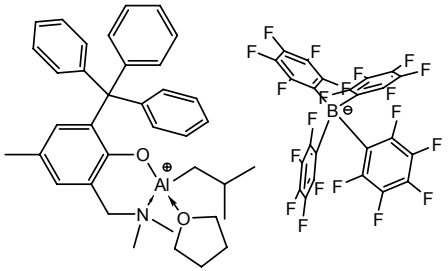
entry	catalyst	initiator	solvent	[M]:[C]:[I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1			none[(a)]	150:0.3:1	60	240 h	no polymerisation				14

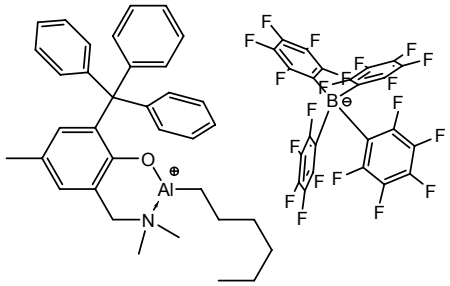
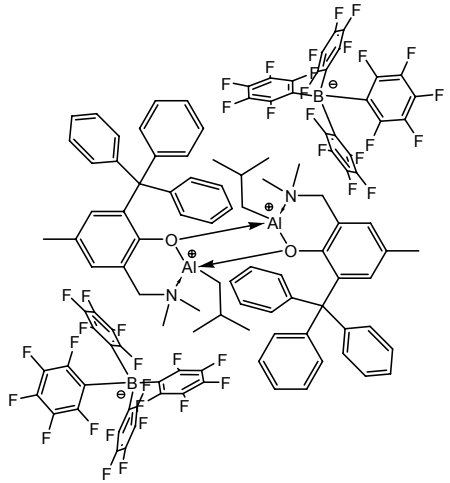
(a) = reaction carried out under normal atmosphere
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator
M = molecular weight
PDI = polydispersity index

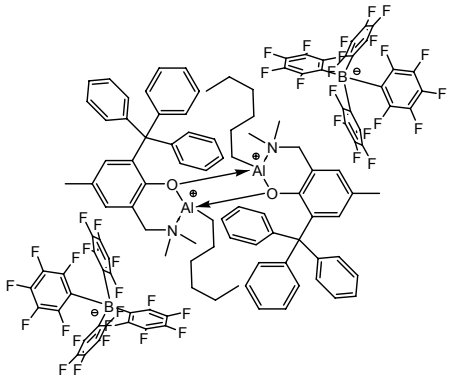
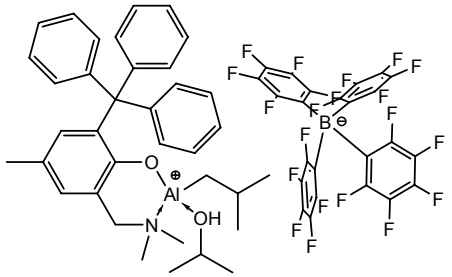
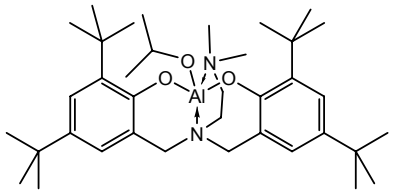
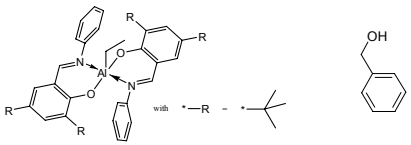
3. Poor metals-based catalysts

Table 2.3 - Selected conditions for the ROP of ε-CL using aluminium-based catalysts that lead to no polymerisation, low conversion or oligomers

entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
1		none	DCM	50:0.3.1	RT	2.5 h		no polymerisation			15
2			toluene	500:1:1	25	20 h		*no polymerisation*			33
3			toluene	50:1	50			*no polymerisation*			34
4			toluene	50:1	50			*no polymerisation*			34
5		none	toluene	100:1	70	24 h		*no polymerisation*			36
6		none	toluene	100:1	70	24 h		*no polymerisation*			36
7		none	toluene	100:1	70	24 h		*no polymerisation*			36

entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
8		none	toluene	100:1	70	24 h		*no polymerisation*			36
9		none	toluene	100:1	25	10 min		*no polymerisation*			37
10			PhBr	120:1	100			*no polymerisation*			42
11			DCM	120:1	40			*no polymerisation*			42

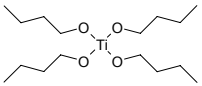
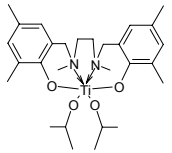
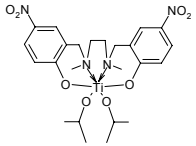
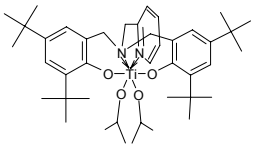
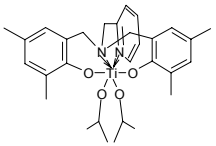
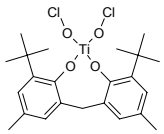
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
12		DCM	120:1	40			*no polymerisation*			[42]
13		DCM	120:1	40			*no polymerisation*			[42]

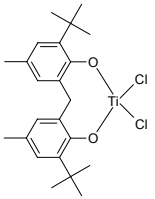
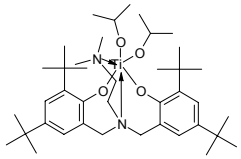
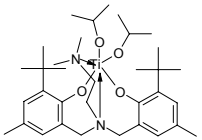
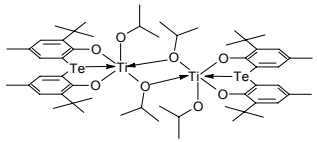
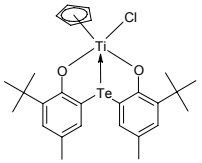
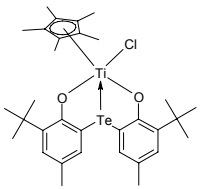
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
14		DCM	120:1	40			*no polymerisation*			42
15		DCM	120:1	40			*no polymerisation*			42
16		DCM	500:1	RT	48 h		*no polymerisation*			22
17		toluene	100:1:1	25	4 h	< 1				37

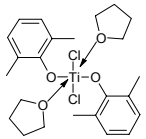
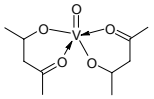
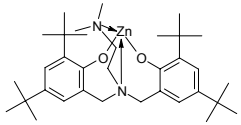
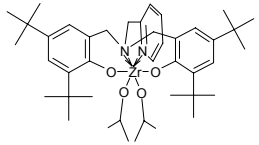
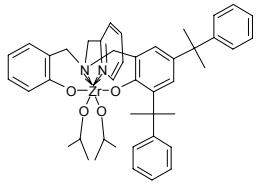
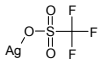
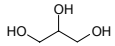
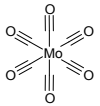
DCM = dichloromethane
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
RT = Room Temperature
M = molecular weight
PDI = polydispersity index

4. Transition metal-based catalysts

Table 2.4 – Chosen conditions for the ROP of ε-CL using transition metal-based catalysts that lead to no polymerisation, low conversion or oligomers

entry	catalyst / initiator	solvent	[M]:[C]:[I] [M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1		toluene	100:1	100	6 h		*low conversion*			62
2		toluene	100:1	RT	24 h		*no polymerisation*			63
3		toluene	100:1	RT	24 h		*no polymerisation*			63
4		toluene	100:1	RT	24 h		*no polymerisation*			63
5		toluene	100:1	RT	24 h		*no polymerisation*			63
6		DCM	100:1	25	24 h		*no polymerisation*			66

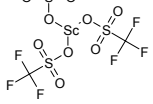
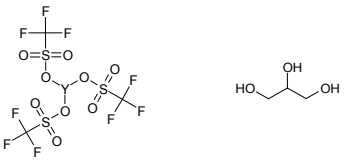
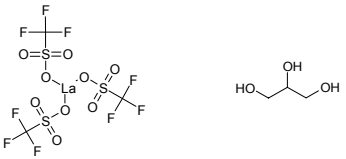
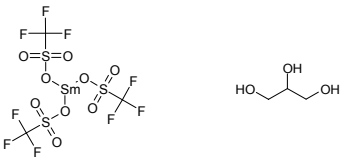
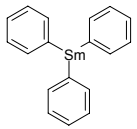
entry	catalyst initiator catalyst/initiator	solvent	[M]:[C]:[I] [M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
7		toluene	200:1	100			*no polymerisation*			67
8		toluene	200:1	60	24 h		*low conversion*			8
9		toluene	200:1	60	24 h		*low conversion*			8
10		toluene	100:1	100	6 h		*low conversion*			62
11		toluene	100:1	100	6 h		*low conversion*			62
12		toluene	100:1	100	6 h		*low conversion*			62

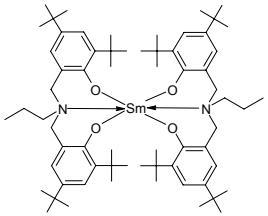
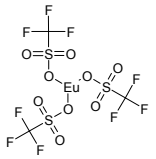
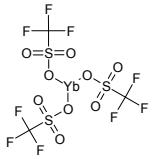
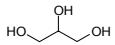
entry	catalyst initiator catalyst/initiator	solvent	[M]:[C]:[I] [M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
13		toluene	100:1	100	6 h		*low conversion*			62
14		methanol$^{(O)}$	67:1	60	24 h		*low conversion*			70
15		toluene	200:1	60	24 h		*low conversion*			8
16		toluene	100:1	RT	24 h		*no polymerisation*			63
17		toluene	100:1	RT	24 h		*no polymerisation*			63
18	 	none	150:0.3:1	60	240 h		46	6,700$^{(n)}$	1.89	14
19		methanol$^{(O)}$	133:1	60	24 h		*no polymerisation*			70

(O) = reaction performed under dioxygen atmosphere, (a) = reaction carried out under normal atmosphere
DCM = dichloromethane, THF = tetrahydrofuran
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
RT = Room Temperature
(MW) = microwave heating
M = molecular weight
(n) = number average molecular weight, (w) = weight average molecular weight
PDI = polydispersity index

5. Rare earth metal-based catalysts

Table 2.5 – Chosen conditions for the ROP of ε-CL using rare earth metal-based catalysts that lead to no polymerisation, low conversion or oligomers

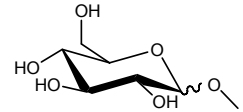
Entry	catalyst / initiator *catalyst/initiator*	Solvent	[M]:[C]:[I] *[M]:[C/I]*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
1a		none[(a)]	150:0.3:1	60	6 h		66	11,400[(n)]	1.66	14
1b	 none	[BMIM][BF_4]	50:1	25	2 days		no polymerisation			79
2		none[(a)]	150:0.03:1	60	48 h		54	13,300[(n)]	1.45	14
3		none[(a)]	150:0.3:1	60	240 h			300[(n)]	2.90	14
4		none[(a)]	50:0.3	60	240 h			300[(n)]	3.50	14
5		THF	125:1	70	2 h			oligomer		2
		Dioxane	125:1	70	2 h			oligomer		2

Entry	catalyst initiator *catalyst/initiator*	Solvent	[M]:[C]:[I] *[M]:[C/I]*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
6		THF	275:1	RT			*no polymerisation*			88
7		none	[BMIM][BF_4]	50:1	25	2 days		*no polymerisation*		79
8			none[(a)]	150:0.3:1	60	240 h		*no polymerisation*		14

(a) = reaction carried out under normal atmosphere
BMIM = 1-butyl-3-methylimidazolium, THF = tetrahydrofuran, DCM = dichloromethane, $scCO_2$ = supercritical carbon dioxide
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
(b) polymer recovered by HCl hydrolysis + decantation ; (c) polymer recovered by MeOH hydrolysis + decantation
RT = Room Temperature
M = molecular weight
(n) = number average molecular weight, (v) = viscosimetric average molecular weight
PDI = polydispersity index

Enzymatic Ring-Opening Polymerisation (eROP)

Table 2.6 – Selected conditions for the eROP of ε-CL that lead to no polymerisation, low conversion or oligomers

entry	catalyst	initiator	solvent	m_M:m_C:m_I	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1	Crude PPL		none	4.1:2.5:1	70	96 h		*no polymerisation*			96

PPL = Porcine Pancreatic Lipase; HLE = Hog Liver Esterase
$scCO_2$ = supercritical carbon dioxide; MTBE = methyl *tert*-butyl ether
m_M = mass of monomer (ε-CL); m_C = mass of catalyst; m_I = mass of initiator
RT = Room Temperature
M = molecular weight
(n) = number average molecular weight, (w) = weight average molecular weight
PDI = polydispersity index

Section 3: Periodic table overview

The different metal catalysts reported in this review are represented in the periodic table as a quick reference guide of studied systems.

	I	II		III	IV	V	VI	VII	VIII
1									
2	LDA PhLi								
3	NaOTf NaC_5H_5	$Mg(OTf)_2$ $Mg(C_3H_5)$(tbpamd) $Mg(^tBu)$(tbpamd) $Mg(CH_2SiMe_3)$(tbpamd) $Mg(C_3H_5)$(pbpamd) $Mg(^tBu)$(pbpamd) $Mg(CH_2SiMe_3)$(pbpamd) [Mg(μ-MEMPEP)(THF)]$_2$ [Mg(μ-MMPEP)(THF)]$_2$ $[(MCIMP)_2Mg_2(THF)]_2$ $Mg[Me_2NC_2H_4N(4,6\text{-}^tBu_2BnO\text{-}3)_2]$		$Al(OTf)_3$ $Et_2AlO(CH_2)_3NH_2$ $AlEt_3$ Et_2AlOMe $Et_2AlOCH_3CHCH_2$ $Al(O^iPr)_3$ $Al(O(CH_2)_2Br)_3$ $Al(O(CH_2)_3CHCH_2)_3$ $Al(O(CH_2)_3NEt_2)_3$ $Et_2AlO(CH_2)_2Br$ $Et_2AlO(CH_2)_3CHCH_2$ $Et_2AlO(CH_2)_3NEt_2$ $AlMe_3$ $MeAl(OPhPh_2)_2$ $MeAl(OPh^tBu_2Me)_2$ $MeAl(OPh^tBu)_2$ $Al(acac)_3$ hapenAlO^iPr $TPPAl(O(CO)CH_2CH(CH_3))_2Cl$ TPPAlOMe TPPAlEt [EDBP]Al(μ-OBn)]$_2$ $[(PhCHO)Al(EDBP)(\mu\text{-}OBn)]_2$ $[(MOBT)_2AlMe]$ $[(MOBT)_2AlCl]$ $[(\mu\text{-}TMBM)AlEt_2]_2$ $[(\mu\text{-}TMBM)Al^iBu_2]_2$ [(MMPEP)-Al(μ-OBn)]$_2$ $[Y(Al(O^iPr)_4)_3]$ [Al(tbmSalen)Cl] [Al(tbmSalen)Me] [Al(tbmSalen)Et] [Al(tbmSalcen)Cl] [Al(tbmSalcen)Me] [Al(tbmSalcen)Et] $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}((2,6\text{-}^iPr_2C_6H_3)N{=}CH)C_6H_3]$ $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(^tBuN{=}CH)C_6H_3]$ $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(C_{10}H_{15}N{=}CH)C_6H_3]$ $Me_2Al[O\text{-}2\text{-}^tBu\text{-}6\text{-}(C_6F_5N{=}CH)C_6H_3]$ $o\text{-}C_6H_4(CH{=}NC_6H_5)(NC_6H_5)AlMe_2$ $o\text{-}C_6H_4(CH{=}N(2,6\text{-}Me_2C_6H_3))(N(2,6\text{-}Me_2C_6H_3)AlMe_2$ $o\text{-}C_6H_4(CH{=}N(2,6\text{-}Et_2C_6H_3))(N(2,6\text{-}Et_2C_6H_3)AlMe_2$ $o\text{-}C_6H_4(CH{=}N(2,6\text{-}^iPr_2C_6H_3))(N(2,6\text{-}Me_2C_6H_3)AlMe_2$ $o\text{-}C_6H_4(CH{=}N(2,6\text{-}^iPr_2C_6H_3))(N(2,6\text{-}Et_2C_6H_3)AlMe_2$ $[^{42}Al(O^iPr)(thf)][B(C_6F_5)_4]$ $[\{2\text{-}(C_6H_5N{=}CH)C_6H_4O\}AlMe_2]$ $(^iPrO)Al\{CH_2NMeCH_2C(CF_3)_2O\}_2$ (^{t}Bu$_2$-BPBA)Al(O-^{i}Pr) (^{t}Bu,OMe-BPBA)Al(O^{i}Pr) (^{t}Bu,Br-BPBA)Al(O^{i}Pr) ...				
4	KO^tBu	$Ca(OMe)_2$ $[Ca(N(SiMe_3))_2(THF)_2]$ $o\text{-}O_2N(C_6H_4)(CH_2)_2OCaNH_2$ H_2NCaO^iPr $[Ca\{Me_2NC_2H_4N(4,6\text{-}^tBu_2BnO\text{-}3)_2\}]_2$							
5		$^iPrOSrNH_2$ $Sr(O^iPr)_2$			$Sn(Oct)_2$ $(^nBu)_3SnOMe$ $(^nBu)_2Sn(OMe)_2$ $(^nBu)_2Sn(Oct)_2$ $(Bn)(OMe)Sn(Ph(^tBu)_3)_2$ $Sn(OTf)_2$ $[Y(Sn(O^iPr)_3)_3]$				
6			cf. f block table Figure						
7									

cf. d block table Figure 3.

tbpamd = *N*-ethyl-*N'*-*tert*-butylbis(3,5-dimethylpyrazol-1-yl)acetamidinate
pbpamd = *N*,*N'*-diisopropylbis(3,5-dimethylpyrazol-1-yl)acetamidinate
tbmSalen = N,N'-l,2-ethylenebis(3-tert-butyl-5-methylsalicylideneimine)
tbmSalcem = N,N'-trans-l,2-cyclohexanediyl-bis(3-tert-butyl-5-methylsalicylideneimine)
MEMPEP-H_2 = 2,2'-(2-methoxybenzylidene)-bis(4,6-di(1-methyl-1-phenylethyl)phenol)
MMPEP-H_2 = 2,2'-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol)
hapen = dichloro[ethylene - N,N' - bis(acetophenone iminato)]
MCIMP-H_2 = 2,2'-methylenebis(4-chloro-6-isopropyl-3-methylphenol)
TPP = 5,10,15,20-tetraphenylporphynato
EDBP-H_2 = 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol)
MOBT-H = 2-methoxybenzenethiol
TMBM-H = 2,4,6-trimethylbenzylmercaptan

Figure 3.1 – Summary of the metal-based catalysts used for the ROP of ε-CL

	d[1]	d[2]	d[3]	d[4]	d[5]	d[6]	d[7]	d[8]	d[9]	d[10]
4	$Sc(OTf)_3$ $PS\text{-}(Ph(CH_2)_5)_2PhSO_2Sc(OTf)_2$	$Ti(O^nBu)_4$ $[(CH_2N(Me)\text{-}4,6\text{-}^tBuBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(CH_2N(Me)\text{-}4,6\text{-}MeBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(CH_2N(Me)\text{-}6\text{-}NO_2BnO\text{-}3)_2]Ti(O^iPr)_2$ $[(Py\text{-}CH_2N(4,6\text{-}^tBuBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(Py\text{-}CH_2N(4,6\text{-}MeBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(MeN(4,6\text{-}^tBuBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(BnN(4,6\text{-}^tBuBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(C_9H_7CH_2N(4,6\text{-}^tBuBnO\text{-}3)_2]Ti(O^iPr)_2$ $[(1,6\text{-}O_2Ph)Ti(O^iPr)_3]_2$ $[(1,6\text{-}O_2Ph)_2Ti(^iPrOH)_2]_2$ $[(1,6\text{-}O_2\text{-}3\text{-}MePh)Ti(O^iPr)_3]_2$ $[(1,6\text{-}O_2\text{-}3\text{-}^tBuPh)Ti(O^iPr)_3]_2$ $[(1,6\text{-}O_2\text{-}2,5\text{-}^tBu_2Ph)Ti(O^iPr)_3]_2$ $[(1,6\text{-}O_2\text{-}3\text{-}MeOPh)Ti(O^iPr)_3]_2$ $[(1,6\text{-}O_2\text{-}3\text{-}NO_2Ph)Ti(O^iPr)_3]_2$ $[(1,6\text{-}O_2\text{-}2\text{-}MePh)Ti(O^iPr)_3]_2$ $(CH_2(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2)Ti(O^iPr)_2$ $(CH_2(3\text{-}PhPhO\text{-}2)_2)Ti(O^iPr)_2$ $(CH_2(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2)Ti(OCl)_2$ $(S(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2Ti(NEt_2)_2$ $(CH_2(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2Ti(NEt_2)_2$ $(CH_2(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2TiCl_2$ $\{Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti\}_2O$ $\{(\eta^5\text{-}^iPrC_5H_4)[\eta^5\text{-}C_5H_3B(C_6F_5)_3]Ti\}_2O$ $[Me_2N(CH_2)_2N(4,6\text{-}^tBu_2BnO\text{-}3)_2]Ti(O^iPr)_2$ $[Me_2N(CH_2)_2N(4\text{-}^tBu\text{-}6\text{-}MeBnO\text{-}3)_2]Ti(O^iPr)_2$ $[Me_2N(CH_2)_2N(4\text{-}^tBu\text{-}6\text{-}MeBnO\text{-}3)_2]Ti(O^iPr)_2(Na)(THF)_2$ $[(S(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2TiCl_2]_2$ $[(Te(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2TiCl_2]_2$ $[(Te(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2Ti(O^iPr)_2]_2$ $[(Te(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2Ti(C_5H_5)Cl]_2$ $[(Te(3\text{-}^tBu\text{-}5\text{-}MePhO\text{-}2)_2Ti(C_5Me_5)Cl]_2$ $[Cl_2Ti(OPh\text{-}2,5\text{-}Me_2)_2(THF)_2]$ $ClTi(O^iPr)_3$ $N((CH_2)_2O)_3TiO^iPr$	$[VO(acac)_2]$ $VOSO_4.H_2O$			$[Fe(OCHPh_2)_2]_2$ $[(Bn(NSiMe_3)_2)_2FeOCHPh_2]$			$Cu(OTf)_2$	$Zn(O^nBu)_2$ $EtZnO(CH_2)_3CHCH_2$ $Zn(O(CH_2)_3CHCH_2)_2$ $EtZnO(CH_2)_2Br$ $Zn(O(CH_2)_2Br)_2$ $Zn(Oct)_2$ $[Me_2N(CH_2)_2N(4\text{-}^tBu\text{-}6\text{-}MeBnO\text{-}3)_2]Zn$ $[(Et_2O)_3ZnCH_2CH_3][B(C_6F_5)_4]$ $[(Et_2O)_3ZnN(SiMe_3)_2][B(C_6F_5)_4]$
5	$Y(OTf)_3$ $Y(O^iPr)_3$ $[Sn(Y(O^iPr)_4)_2]$ YPh_3 $[Cp_2YOMe]_2$ $[Cp_2YOMe(THF)]$ $Y(N(SiMe_3)_2)_3$ $Y(O\text{-}2,6\text{-}^tBu_2Ph)_3$	$Zr(O^nBu)_4$ $Zr(acac)_4$ $[(CH_2N(Me)\text{-}4,6\text{-}MeBnO\text{-}3)_2]Zr(O^iPr)_2$ $[(CH_2N(Me)\text{-}4,6\text{-}^tBuBnO\text{-}3)_2]Zr(O^iPr)_2$ $[(Py\text{-}CH_2N(4,6\text{-}MeBnO\text{-}3)_2]Zr(O^iPr)_2$ $[(Py\text{-}CH_2N(4,6\text{-}^tBuBnO\text{-}3)_2]Zr(O^iPr)_2$ $[(Py\text{-}CH_2N(BnO\text{-}3)(4,6\text{-}C(CH_3)_2PhBnO\text{-}3)]Zr(O^iPr)_2$ $[(C_4H_4N)_2Zr(C_4H_4N\text{-}CH_2NEt_2)_2]$ $[(2,6\text{-}MePhO)_2Zr(C_4H_4N\text{-}CH_2NEt_2)_2]$ $[(2,6\text{-}^tBuPhO)_2Zr(C_4H_4N\text{-}CH_2NEt_2)_2]$		$H_5[PMo_{10}V_2O_{40}]$ $H_3[PMo_{12}O_{40}]$ $H_6[PMo_9V_3O_{40}]$ $[MoO_2(acac)_2]$ $Mo(CO)_6$					AgOTf	
6	$La(OTf)_3$ $La(O^iPr)_3$ $La(O\text{-}2,4\text{-}^tBu_2\text{-}6\text{-}(CHNPy)Ph)_3$	$[(C_4H_4N)_2Hf(C_4H_4N\text{-}CH_2NEt_2)_2]$ $[(2,6\text{-}MePhO)_2Hf(C_4H_4N\text{-}CH_2NEt_2)_2]$ $[(2,6\text{-}^tBuPhO)_2Hf(C_4H_4N\text{-}CH_2NEt_2)_2]$		$H_3[PW_{12}O_{40}]$						
7										

Figure 3.2 – Summary of the metal-based catalysts used for the ROP of ε-CL, d-block

	f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}
6	$Ce(OTf)_4$		$Nd(OTf)_3$ $NdPh_3$ $Nd(O^iPr)_3$		$Sm(OTf)_3$ $SmPh_3$ $Sm(O^iPr)_3$ $Sm(N(SiMe_3)_2)_3$ $[ClSm(N(SiMe_3)_2)_2(THF)]_2$ $[BrSm(N(SiMe_3)_2)_2(THF)]_2$ $Sm(O\text{-}2,6\text{-}^tBu\text{-}4\text{-}MePh)_2(THF)_3$ $[(C_5Me_5)Sm(\mu\text{-}O\text{-}2,6\text{-}^tBu\text{-}4\text{-}MePh)]_2$ $[(C_5Me_5)_2SmH]_2$ $[(C_5Me_5)_2SmOEt(OEt_2)]$ $[(MeO(CH_2)_2N(4,6\text{-}^tBuBnO\text{-}3)_2)_2Sm]$ $[(Me_2N(CH_2)_2N(4,6\text{-}^tBuBnO\text{-}3)_2)_2Sm]$ $[(^nPrN(4,6\text{-}^tBuBnO\text{-}3)_2)_2Sm]$ $[(Me_2N(CH_2)_2N(4,6\text{-}^tBuBnO\text{-}3)_2)SmN(SiMe_3)_2]$	$Eu(OTf)_3$	$Gd(OTf)_3$						$Yb(OTf)_3$ $[(C_5Me_5)_2YbH]_2$	$Lu(OTf)_3$
7														

Figure 3.3 – Summary of the metal-based catalysts used for the ROP of ε-CL, f bloc

1. A. Bhaw-Luximon, D. Jhurry, S. Motala-Timol and Y. Lochee, *Macromol. Symp.*, 2006, **231**, 60-68.
2. X. Deng, M. Yuan, C. Xiong and X. Li, *J. Appl. Polym. Sci.*, 1999, **73**, 1401-1408.
3. M. Yuan, C. Xiong and X. Deng, *J. Appl. Polym. Sci.*, 1998, **67**, 1273-1276.
4. A.-F. Mingotaud, F. Dargelas and F. Cansell, *Macromol. Symp.*, 2000, **153**, 77-86.
5. L. F. Sanchez-Barba, A. Garces, M. Fajardo, C. Alonso-Moreno, J. Fernandez-Baeza, A. Otero, A. Antinolo, J. Tejeda, A. Lara-Sanchez and M. I. Lopez-Solera, *Organometallics*, 2007, **26**, 6403-6411.
6. T.-L. Yu, C.-C. Wu, C.-C. Chen, B.-H. Huang, J. Wu and C.-C. Lin, *Polymer*, 2005, **46**, 5909-5917.
7. M.-L. Shueh, Y.-S. Wang, B.-H. Huang, C.-Y. Kuo and C.-C. Lin, *Macromolecules*, 2004, **37**, 5155-5162.
8. Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.*, 2006, 340-350.
9. Z. Zhong, M. J. K. Ankoné, P. J. Dijkstra, C. Birg, M. Westerhausen and J. Feijen, *Polym. Bull.*, 2001, **46**, 51-57.
10. Z. Zhong, P. J. Dijkstra, C. Birg, M. Westerhausen and J. Feijen, *Macromolecules*, 2001, **34**, 3863-3868.
11. G. Rong, M. Deng, C. Deng, Z. Tang, L. Piao, X. Chen and X. Jing, *Biomacromolecules*, 2003, **4**, 1800-1804.
12. L. Piao, M. Deng, X. Chen, L. Jiang and X. Jing, *Polymer*, 2003, **44**, 2331-2336.
13. Z. Tang, X. Chen, Q. Liang, X. Bian, L. Yang, L. Piao and X. Jing, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 1934-1941.
14. Y. Wang and M. Kunioka, *Macromol. Symp.*, 2005, **224**, 193-206.
15. M. Akatsuka, T. Aida and S. Inoue, *Macromolecules*, 1995, **28**, 1320-1322.
16. Z. Florjanczyk, A. Plichta and M. Sobczak, *Polymer*, 2006, **47**, 1081-1090.
17. P. Dubois, P. Degee, R. Jerome and P. Teyssie, *Macromolecules*, 1992, **25**, 2614-2618.
18. A. Duda, Z. Florjanczyk, A. Hofman, S. Slomkowski and S. Penczek, *Macromolecules*, 1990, **23**, 1640-1646.
19. H. R. Kricheldorf, M. Berl and N. Scharnagl, *Macromolecules*, 1988, **21**, 286-293.
20. C. Jacobs, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 1991, **24**, 3027-3034.
21. D. Tian, P. Dubois and R. Jerome, *Macromolecules*, 1997, **30**, 2575-2581.
22. A. Amgoune, L. Lavanant, C. M. Thomas, Y. Chi, R. Welter, S. Dagorne and J.-F. Carpentier, *Organometallics*, 2005, **24**, 6279-6282.
23. V. Bergeot, T. Tassaing, M. Besnard, F. Cansell and A.-F. Mingotaud, *J. Supercritical Fluids*, 2004, **28**, 249-261.
24. C. Miola-Delaite and T. H. R. Spitz, *Macromol. Chem. Phys.*, 1999, **200**, 1771-1778.
25. A. Duda, *Macromolecules*, 1996, **29**, 1399-1406.
26. A. Duda, S. Penczek, P. Dubois, D. Mecerreyes and R. Jérôme, *Macromol. Chem. Phys.*, 1996, **197**, 1273-1283.
27. A. Duda and S. Penczek, *Macromolecules*, 1995, **28**, 5981-5992.
28. N. Ropson, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 1993, **26**, 6378-6385.
29. E. Martin, P. Dubois and R. Jérôme, *Macromolecules*, 2003, **36**, 7094-7099.
30. P. Dubois, N. Ropson, R. Jerome and P. Teyssie, *Macromolecules*, 1996, **29**, 1965-1975.
31. A. Kowalski, J. Libiszowski, K. Majerska, A. Duda and S. Penczek, *Polymer*, 2007, **48**, 3952-3960.
32. S. Motala-Timol and D. Jhurry, *Polym. Int.*, 2007, **56**, 1053-1062.
33. A. Arbaoui, C. Redshaw and D. L. Hughes, *Chem. Commun.*, 2008, 4717-4719.

34. I. Taden, H.-C. Kang, W. Massa and J. Okuda, *J. Org. Chem.*, 1997, **540**, 189-192.
35. N. Iwasa, J. Liu and K. Nomura, *Catal. Commun.*, 2008, **9**, 1148-1152.
36. W. Yao, Y. Mu, A. Gao, Q. Su, Y. Liu and Y. Zhang, *Polymer*, 2008, **49**, 2486-2491.
37. N. Nomura, T. Aoyama, R. Ishii and T. Kondo, *Macromolecules*, 2005, **38**, 5363-5366.
38. M. Endo, T. Aida and S. Inoue, *Macromolecules*, 1987, **20**, 2982-2988.
39. B.-T. Ko and C.-C. Lin, *Macromolecules*, 1999, **32**, 8296-8300.
40. C.-H. Huang, F.-C. Wang, B.-T. Ko, T.-L. Yu and C.-C. Lin, *Macromolecules*, 2001, **34**, 356-361.
41. Y.-C. Liu, B.-T. Ko and C.-C. Lin, *Macromolecules*, 2001, **34**, 6196-6201.
42. S. Dagorne, F. Le Bideau, R. Welter, S. Bellemin-Laponnaz and A. Maisse-François, *Chemistry - A European Journal*, 2007, **13**, 3202-3217.
43. L. M. Alcazar-Roman, B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2003, 3082-3087.
44. A. C. Albertsson and M. Gruvegård, *Polymer*, 1995, **36**, 1009-1016.
45. E. Helwig, B. Sandner, U. Gopp, F. Vogt, S. Wartewig and S. Henning, *Biomaterials*, 2001, **22**, 2695-2702.
46. A. Kowalski, A. Duda and S. Penczek, *Macromol. Rapid Commun.*, 1998, **19**, 567-572.
47. A. Duda, S. Penczek, A. Kowalski and J. Libiszowski, *Macromol. Symp.*, 2000, **153**, 41-53.
48. B. Kiskan and Y. Yagci, *Polymer*, 2005, **46**, 11690-11697.
49. M. Degirmenci, O. Izgin and Y. Yagci, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3365-3372.
50. M. Degirmenci, G. Hizal and Y. Yagci, *Macromolecules*, 2002, **35**, 8265-8270.
51. D. Bratton, M. Brown and S. M. Howdle, *Macromolecules*, 2005, **38**, 1190-1195.
52. A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 2000, **33**, 689-695.
53. J. Libiszowski, A. Kowalski, A. Duda and S. Penczek, *Macromol. Chem. Phys.*, 2002, **203**, 1694-1701.
54. A. D. Celiz and O. A. Scherman, *Macromolecules*, 2008, **41**, 4115-4119.
55. M. Möller, R. Kånge and J. L. Hedrick, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2067-2074.
56. A. Kowalski, J. Libiszowski, T. Biela, M. Cypryk, A. Duda and S. Penczek, *Macromolecules*, 2005, **38**, 8170-8176.
57. F. Stassin, O. Halleux and R. Jerome, *Macromolecules*, 2001, **34**, 775-781.
58. F. Stassin and R. Jerome, *Chem. Commun.*, 2003, 232-233.
59. D. Pappalardo, L. Annunziata, C. Pellecchia, M. Biesemans and R. Willem, *Macromolecules*, 2007, **40**, 1886-1890.
60. M. Möller, F. Nederberg, L. S. Lim, R. Kange, C. J. Hawker, J. L. Hedrick, Y. Gu, R. Shah and N. L. Abbott, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 3529-3538.
61. P. Albert, H. Warth, R. Mülhaupt and R. Janda, *Macromol. Chem. Phys.*, 1996, **197**, 1633-1641.
62. Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, H. Yasuda, A. Harada and J. Okuda, *Macromolecules*, 2002, **35**, 7538-7544.
63. A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250-7257.
64. A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2006, 887-889.
65. M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Inorg. Chem.*, 2006, **45**, 2282-2287.
66. D. Takeuchi, T. Nakamura and T. Aida, *Macromolecules*, 2000, **33**, 725-729.
67. Y. Takashima, Y. Nakayama, T. Hirao, H. Yasuda and A. Harada, *J. Org. Chem.*, 2004, **689**, 612-619.
68. V. V. Burlakov, A. V. Letov, P. Arndt, W. Baumann, A. Spannenberg, C. Fischer, L. I. Strunkina, M. K. Minacheva, Y. S. Vygodskii, U. Rosenthal and V. B. Shur, *J. Mol. Catal. A: Chem.*, 2003, **200**, 63-67.
69. Y. Kim, G. K. Jnaneshwara and J. G. Verkade, *Inorg. Chem.*, 2003, **42**, 1437-1447.
70. Y. Mahha, A. Atlamsani, J.-C. Blais, M. Tessier, J.-M. Brégeault and L. Salles, *J. Mol. Catal. A: Chem.*, 2005, **234**, 63-73.
71. B. J. O'Keefe, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 4384-4393.
72. L. Liao, L. Liu, C. Zhang and S. Gong, *Macromol. Rapid Commun.*, 2006, **27**, 2060-2064.
73. I. Barakat, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 1991, **24**, 6542-6545.
74. A. Duda, A. Kowalski, S. Penczek, H. Uyama and S. Kobayashi, *Macromolecules*, 2002, **35**, 4266-4270.
75. Y. Sarazin, M. Schormann and M. Bochmann, *Organometallics*, 2004, **23**, 3296-3302.
76. P. Dobrzynski, *Polymer*, 2007, **48**, 2263-2279.
77. K.-C. Hsieh, W.-Y. Lee, L.-F. Hsueh, H. M. Lee and J.-H. Huang, *Eur. J. Inorg. Chem.*, 2006, **2006**, 2306-2312.
78. N. Nomura, A. Taira, T. Tomioka and M. Okada, *Macromolecules*, 2000, **33**, 1497-1499.
79. N. Nomura, A. Taira, A. Nakase, T. Tomioka and M. Okada, *Tetrahedron*, 2007, **63**, 8478-8484.
80. A. Takasu, M. Oshimura and T. Hirabayashi, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 2300-2304.
81. X. M. Deng, Z. Zhu, C. Xiong and L. Zhang, *J. Appl. Polym. Sci.*, 1997, **64**, 1295-1299.
82. M. Yamashita, Y. Takemoto, E. Ihara and H. Yasuda, *Macromolecules*, 1996, **29**, 1798-1806.
83. E. Martin, P. Dubois and R. Jerome, *Macromolecules*, 2000, **33**, 1530-1535.
84. W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra and J. Feijen, *Macromolecules*, 1996, **29**, 3332-3333.
85. W. Lin, W. L. Sun and Z. Q. Shen, *Chin. Chem. Lett.*, 2007, **18**, 1133-1136.
86. S. Agarwal, M. Karl, K. Dehnicke, G. Seybert, W. Massa and A. Greiner, *J. Appl. Polym. Sci.*, 1999, **73**, 1669-1674.
87. M. Nishiura, Z. Hou, T.-a. Koizumi, T. Imamoto and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 8245-8251.
88. H. E. Dyer, S. Huijser, A. D. Schwarz, C. Wang, R. Duchateau and P. Mountford, *Dalton Trans.*, 2008, 32-35.
89. R. T. MacDonald, S. K. Pulapura, Y. Y. Svirkin, R. A. Gross, D. L. Kaplan, J. Akkara, G. Swift and S. Wolk, *Macromolecules*, 1995, **28**, 73-78.

90. G. A. R. Nobes, R. J. Kazlauskas and R. H. Marchessault, *Macromolecules*, 1996, **29**, 4829-4833.
91. S. Kobayashi, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 3041-3056.
92. S. Kobayashi, H. Uyama and S. Namekawa, *Polym. Degrad. Stab.*, 1998, **59**, 195-201.
93. S. Kobayashi, K. Takeya, S. Suda and H. Uyama, *Macromol. Chem. Phys.*, 1998, **199**, 1729-1736.
94. H. Uyama, K. Takeya and S. Kobayashi, *Proc. Jpn. Acad., Ser. B*, 1993, **69**, 203-207.
95. G. Sivalingam and G. Madras, *Biomacromolecules*, 2004, **5**, 603-609.
96. K. S. Bisht, F. Deng, R. A. Gross, D. L. Kaplan and G. Swift, *J. Am. Chem. Soc.*, 1998, **120**, 1363-1367.
97. H. Uyama, K. Takeya and S. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 56-61.
98. H. Uyama, K. Takeya, N. Hoshi and S. Kobayashi, *Macromolecules*, 1995, **28**, 7046-7050.
99. M. L. Foresti and M. L. Ferreira, *Macromol. Rapid Commun.*, 2004, **25**, 2025-2028.
100. H. Uyama, S. Suda, H. Kikuchi and S. Kobayashi, *Chem. Lett.*, 1997, **26**, 1109-1110.
101. A. Córdova, T. Iversen, K. Hult and M. Martinelle, *Polymer*, 1998, **39**, 6519-6524.
102. A. Kumar and R. A. Gross, *Biomacromolecules*, 2000, **1**, 133-138.
103. F. C. Loeker, C. J. Duxbury, R. Kumar, W. Gao, R. A. Gross and S. M. Howdle, *Macromolecules*, 2004, **37**, 2450-2453.
104. C. Hedfors, E. Ostmark, E. Malmstrom, K. Hult and M. Martinelle, *Macromolecules*, 2005, **38**, 647-649.
105. Y. Mei, A. Kumar and R. A. Gross, *Macromolecules*, 2002, **35**, 5444-5448.
106. A. Cordova, T. Iversen and K. Hult, *Macromolecules*, 1998, **31**, 1040-1045.
107. H. Dong, H.-d. Wang, S.-g. Cao and J.-c. Shen, *Biotechnol. Lett.*, 1998, **20**, 905-908.
108. H. Dong, Z. Wang, Z.-Q. Li, D.-L. You, S.-P. Han, S.-G. Cao and J.-C. Shen, *Ann. N. Y. Acad. Sci.*, 1998, **864**, 263-266.
109. H. Dong, S.-G. Cao, Z.-Q. Li, S.-P. Han, D.-L. You and J.-C. Shen, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1265-1275.
110. B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 8574-8583.
111. R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2006, **128**, 4556-4557.
112. J. Casas, P. V. Persson, T. Iversen and A. Cordova, *Advances in Synthesis & Catalysis*, 2004, **346**, 1087-1089.
113. P. V. Persson, J. Schroder, K. Wickholm, E. Hedenstrom and T. Iverson, *Macromolecules*, 2004, **37**, 5889-5893.
114. J. Hafren and A. Cordova, *Macromol. Rapid Commun.*, 2005, **26**, 82-86.
115. Y. Shibasaki, H. Sanada, M. Yokoi, F. Sanda and T. Endo, *Macromolecules*, 2000, **33**, 4316-4320.
116. S. Gazeau-Bureau, D. Delcroix, B. Martin-Vaca, D. Bourissou, C. Navarro and S. Magnet, *Macromolecules*, 2008, **41**, 3782-3784.
117. M. Basko and P. Kubisa, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 7071-7081.
118. L. Zhang, F. Nederberg, R. C. Pratt, R. M. Waymouth, J. L. Hedrick and C. G. Wade, *Macromolecules*, 2007, **40**, 4154-4158.
119. E. F. Connor, G. W. Nyce, M. Myers, A. Mock and J. L. Hedrick, *J. Am. Chem. Soc.*, 2002, **124**, 914-915.