Supplementary Material (ESI) for Chemical Society Reviews

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

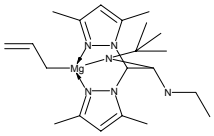
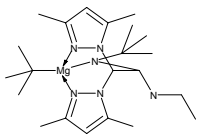
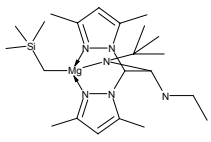
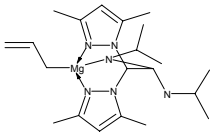
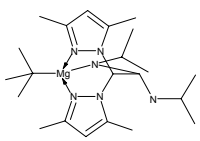
Table 1.1 - Conditions for the ROP of ε-CL using alkali-based catalysts, and characteristics of the resulting PCL

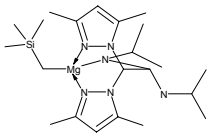
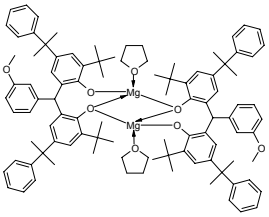
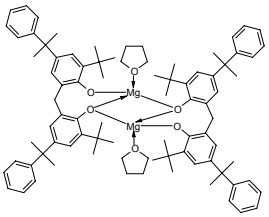
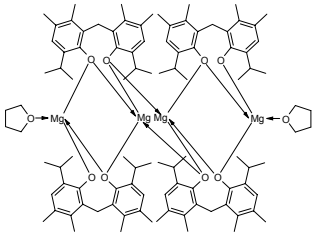
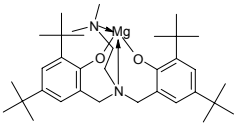
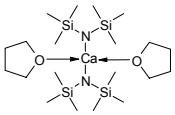
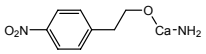
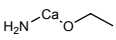
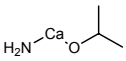
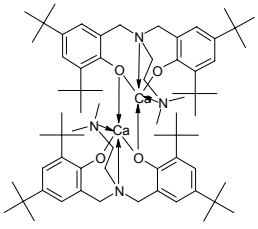
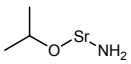
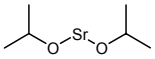
Entry	Catalyst/Initiator	solvent	[M]:[C/I]	T (°C)	reaction time	conv. (%)	yield (%)	M_n (g/mol)	PDI	Ref
1		dioxane	50:1	25	5 min	100		5,700		[1]
2		none	100:1	180	120 min		89	77,000		[2]
3		none	250:1	20	10 min	93		12,100		[3]
		toluene	250:1	20	1 h	98		11,600		[3]
		benzene	250:1	20	1 h	96		10,700		[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

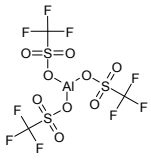
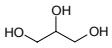
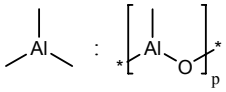
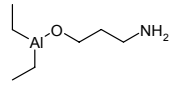
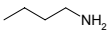
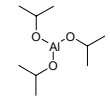
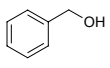
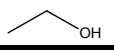
THF = tetrahydrofuran

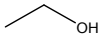
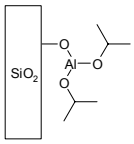
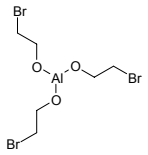
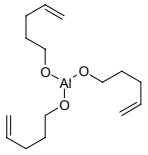
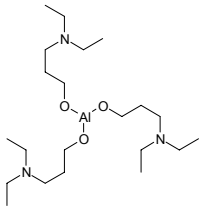
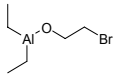
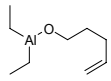
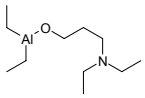
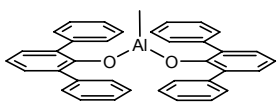
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst/initiator
M = molecular weight
(n) = number average molecular weight, (v) = viscosimetric average molecular weight, (w) = weight average molecular weight
PDI = polydispersity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

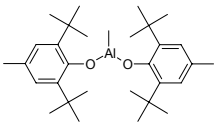
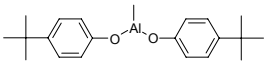
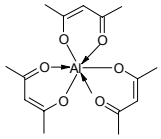
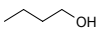
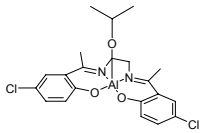
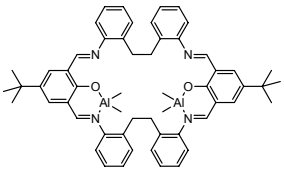
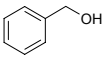
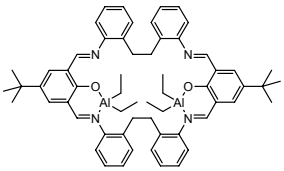
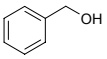
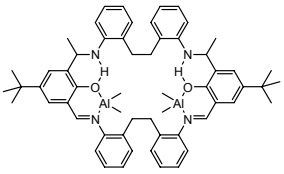
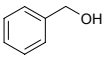
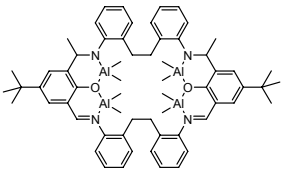
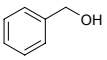
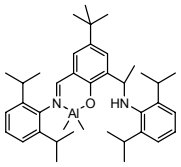
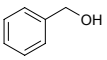
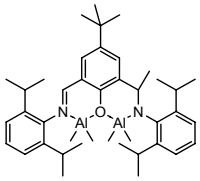
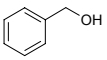
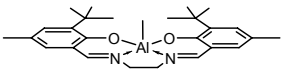
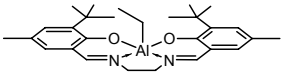
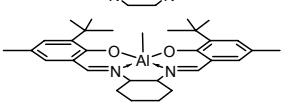
3. Poor metals-based catalysts

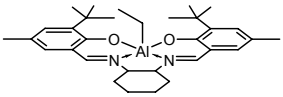
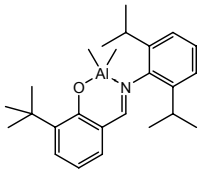
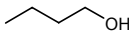
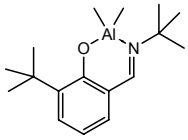
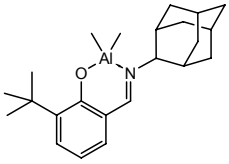
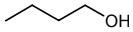
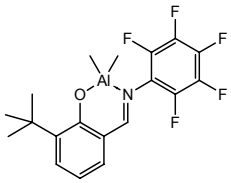
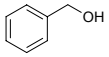
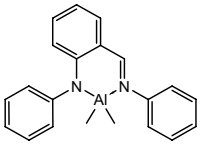
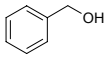
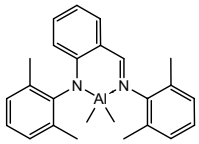
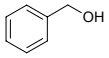
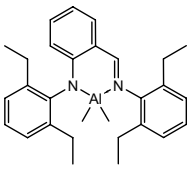
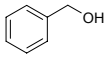
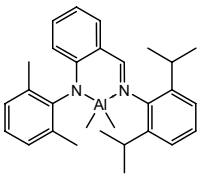
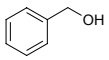
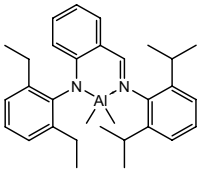
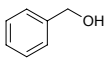
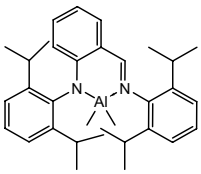
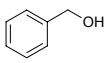
a. Aluminium-based catalysts

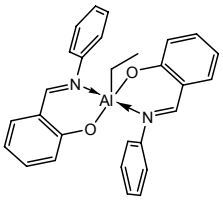
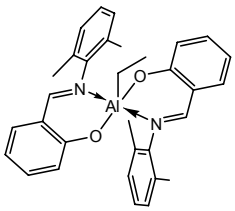
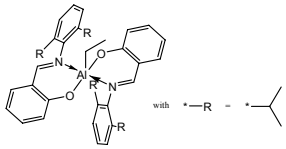
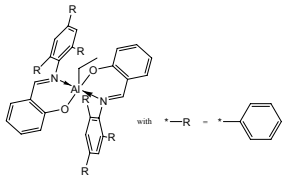
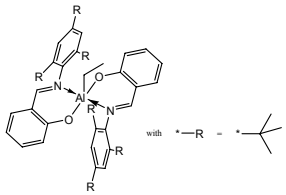
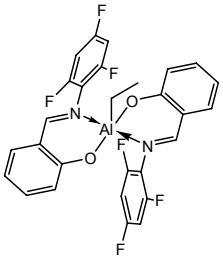
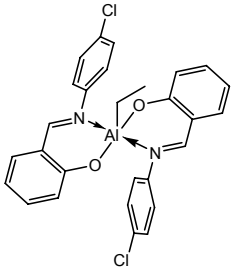
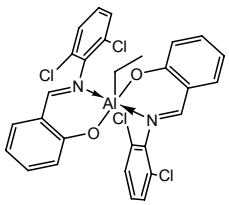
Table 1.3 - Selected conditions for the ROP of ε-CL using aluminium-based catalysts, and characteristics of the resulting PCL

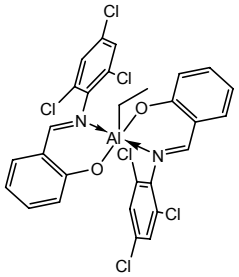
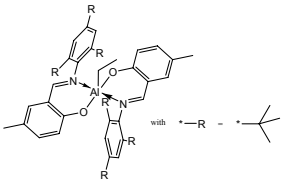
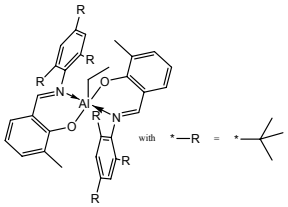
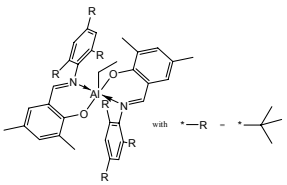
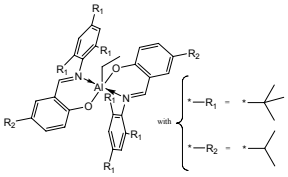
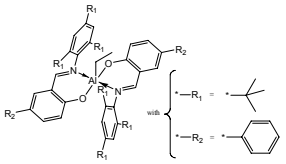
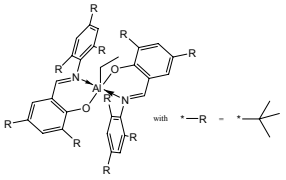
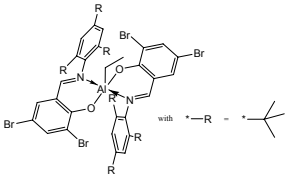
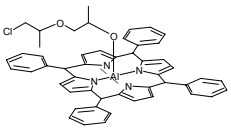
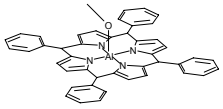
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
1			none[(a)]	120:0.3:1	60	6 h		89	18,400	1.94	14
2			DCM	50:0.3:1	RT	1 h	94		6,000	1.35	15
3	 90:10		toluene	25:1	60	20 h	89		2,900[(n)]		16
4			toluene		40		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

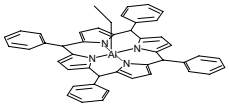
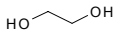
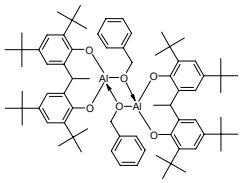
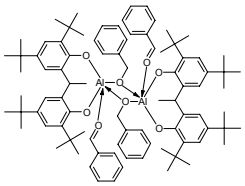
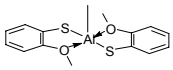
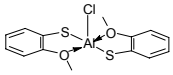
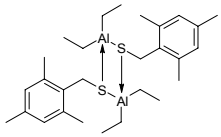
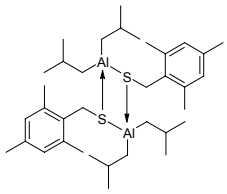
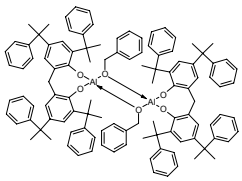
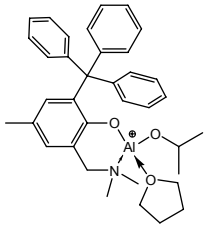
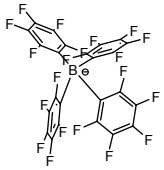
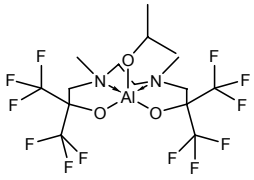
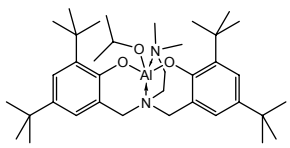
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
9e	A_3:A_4 = 100:0	none	toluene	333:1	20	0.2 h	100		12,200$^{(n)}$	1.10	26
			THF	3000:1	25	1000 min			108,000$^{(n)}$	1.03	27
9f	A_3:A_4 = 95:5	none	THF	571:1	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

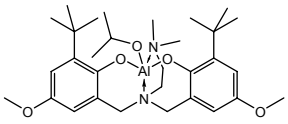
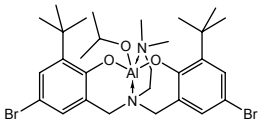
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
18			DCM	50:0.3:1	RT	5 h	95		6,300	1.27	15
19			DCM	50:0.3:1	RT	2 h	100		6,800	1.22	15
20			THF	10:0.25:1	80		≈100		1,290		31
21			DCM	50:1	25	3 h	100		6,600		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]

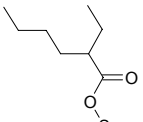
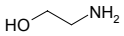
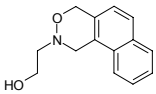
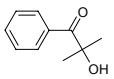
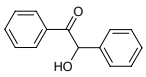
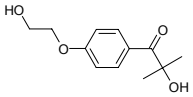
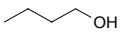
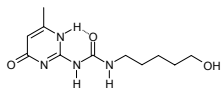
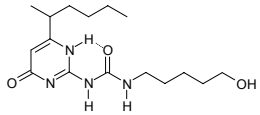
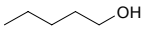
entry	catalyst *(catalyst/initiator)*	initiator	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
60			none	200:1:1	50	21 days	49		10,400	1.18	[38]
				200:1:1	50	24 days	100		2,600	1.12	[38]
61a		none	toluene	200:1	25	48 h		95	43,900	1.15	[39]
61b			toluene	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]

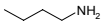
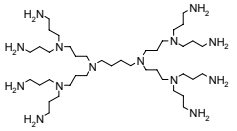
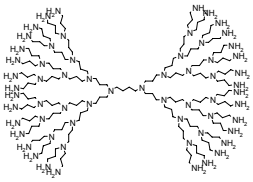
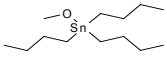
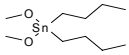
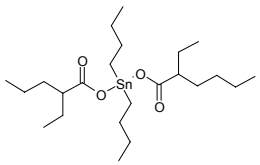
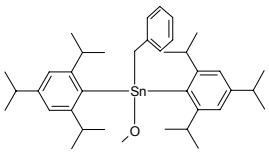
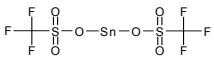
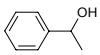
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref.
71		toluene	100:1	25			Similar than above			43
72		toluene	100:1	25			Similar than above			43

(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

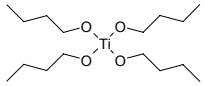
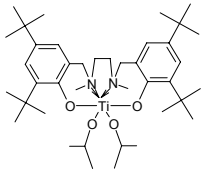
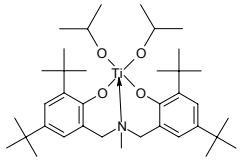
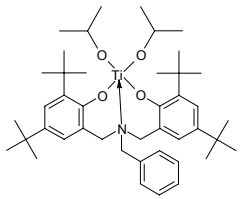
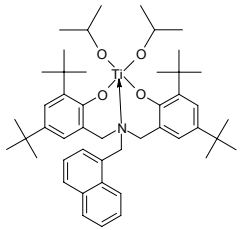
entry	catalyst Initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1a	 None	none	667:1	110				92,000$^{(n)}$	1.77	44
			286:1	130	93 min	98.6		25,300$^{(n)}$	1.57	45
		THF	40:1	80				283,000$^{(n)}$	1.40	46, 47
1b		dioxane	50:1:1	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

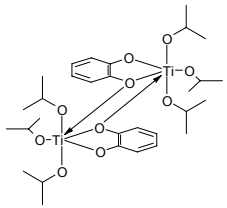
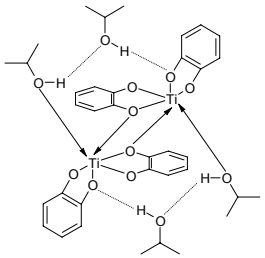
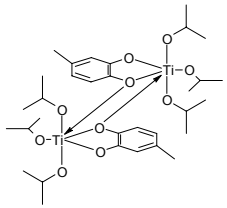
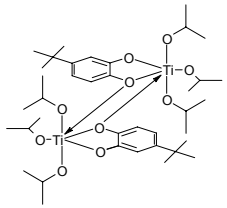
entry	catalyst / Initiator (catalyst/initiator)	solvent	[M]:[C]:[I] ([M]:[C/I])	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1m		none	30:0.01:1	110	24 h		84	3,500	1.18	55
1n		THF	100:15:1	80						56
1o		THF	858:0.9:1	80				79,000(n)	1.04	56
1p		THF	2607:2.6:1	80				287,500(n)	1.05	56
1q	$Ca_5(PO_4)_3(OH)$	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

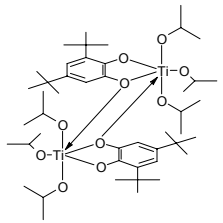
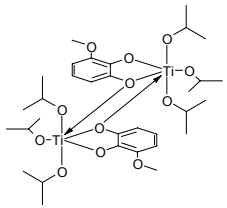
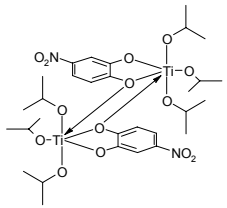
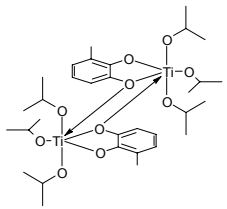
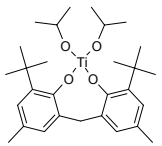
THF = tetrahydrofuran, $scCO_2$ = supercritical carbon dioxide, CFC-113 = 1,1,2-trichloro-1,2,2-trifluoroethane
[M] = concentration of monomer (ε-CL); [C] = concentration of catalyst; [I] = concentration of initiator; [C/I] = concentration of catalyst
M = molecular weight
(n) = number average molecular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

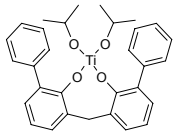
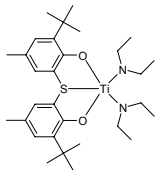
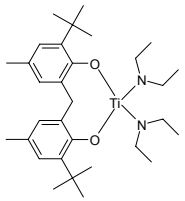
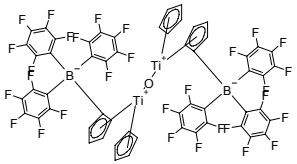
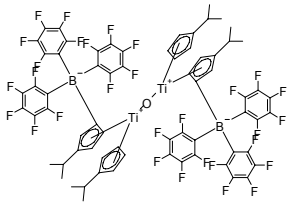
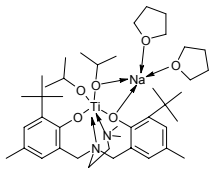
4. Transition metal-based catalysts

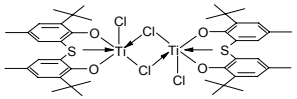
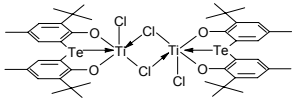
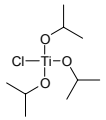
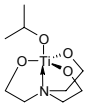
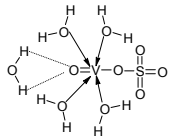
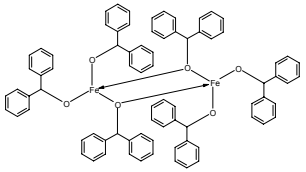
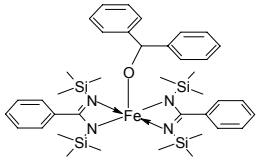
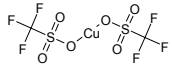
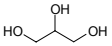
Table 1.5 – Chosen conditions for the ROP of ε-CL using transition metal-based catalysts, and characteristics of the resulting PCL

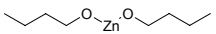
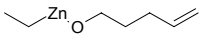
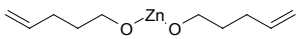
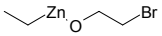
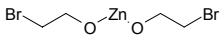
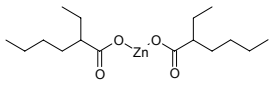
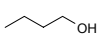
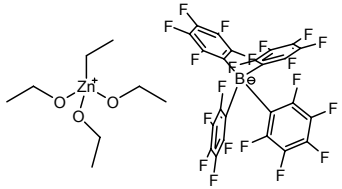
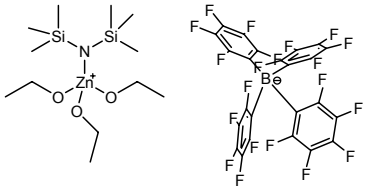
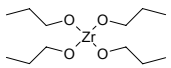
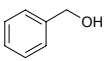
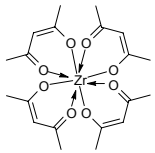
entry	catalyst / initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
1		none	400:1	100	24 h		93	$10,843^{(n)}$		19
			4400:1	180	15 min	90		$90,000^{(n)}$		61
		toluene	100:1	100	6 h		low conversion			62
2		toluene	100:1	RT	24 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

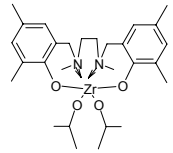
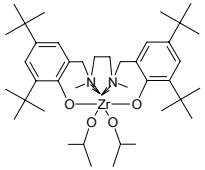
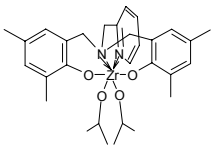
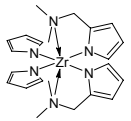
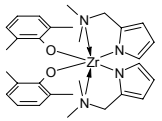
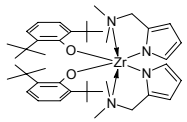
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
6		toluene	100:1	20	24 h		79	2,100$^{(n)}$	1.19	[65]
7		toluene	100:1	20	24 h		25	1,300$^{(n)}$	1.22	[65]
8		toluene	100:1	20	24 h		61	2,600$^{(n)}$	1.20	[65]
9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

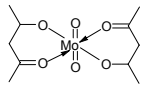
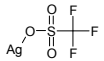
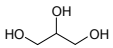
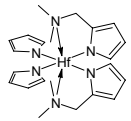
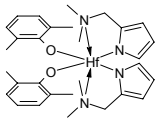
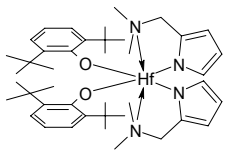
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
10		toluene	100:1	20	24 h		71	3,500$^{(n)}$	1.27	[65]
11		toluene	100:1	20	24 h		4	1,300$^{(n)}$	1.24	[65]
12		toluene	100:1	20	24 h		29	1,500$^{(n)}$	1.18	[65]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

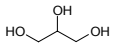
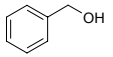
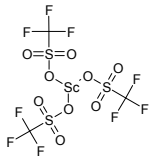
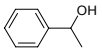
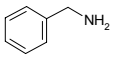
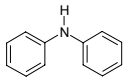
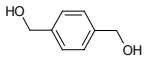
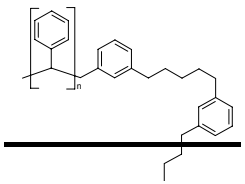
entry	catalyst initiator *(catalyst/initiator)*	solvent	[M]:[C]:[I] *([M]:[C/I])*	T (°C)	reaction time	conv. (%)	yield (%)	M (g/mol)	PDI	Ref
40		toluene	100:1	RT	24 h		> 99	6,000$^{(n)}$	2.60	63
41		toluene	100:1	RT	24 h		10	1,000$^{(n)}$	1.59	63
42		toluene	100:1	RT	24 h		> 99	7,500$^{(n)}$	1.27	63
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