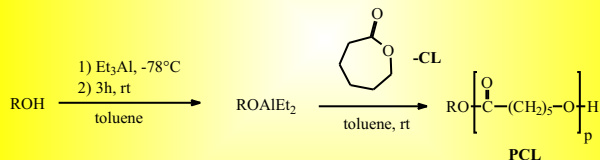


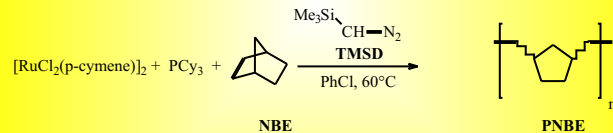
Ring Opening Polymerization (ROP)

The living Ring Opening Polymerization (ROP) of ϵ -caprolactone initiated by aluminum alkoxides is a well-known process to synthesize poly- ϵ -caprolactone (PCL).¹



Ring Opening Metathesis Polymerization (ROMP)

Recently, ruthenium carbene complexes have been shown to initiate the Ring Opening Metathesis Polymerization (ROMP) of cyclic olefins such as norbornene (NBE) derivatives.^{2,3} For this purpose, a catalyst $[Ru]=CHSiMe_3$ generated "in situ" from Me_3SiCHN_2 , $[RuCl_2(p\text{-cymene})_2]$, and PCy_3 , has been developed in our laboratory.²

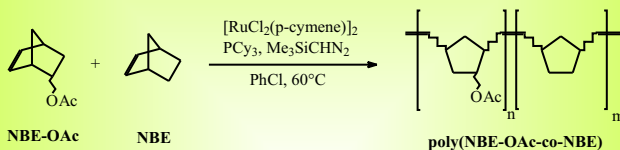


Combination of ROP and ROMP

Well-defined poly(NBE-g- ϵ -CL) copolymers have been prepared using either the "grafting from"⁴ or the macromonomer⁵ technique.

"Grafting from" technique

Synthesis of poly(NBE-OAc-co-NBE)

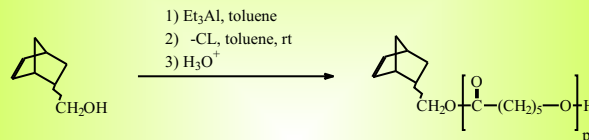


[NBE]/[NBE-OAc] ₀	[M] ₀ /[Ru] ₀	Time (min)	[M] ₀ (mol l ⁻¹)	Yield %	Mn* (SEC)	M _w /M _n	Mol % NBE-OAc (H NMR)
0/100	94	60	0.047	45	77,000	1.2	100
60/40	133	10	0.132	76	92,000	1.1	28
82/18	133	0.5	0.088	90	125,000	1.2	3
94/6	133	0.5	0.088	90	125,000	1.2	3
94/6	266	0.5	0.088	90	257,000	1.4	3

*Polystyrene standards

Macromonomer technique

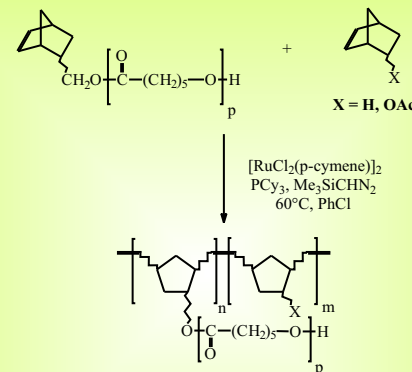
Synthesis of macromonomers



Code	Reaction time (h)	Yield %	Mn (theor)	Mn ('H NMR)	Mn* (SEC)	M _w /M _n
1	13	85	2,500	2,000	2,100	1.10
2	17	95	3,300	3,200	2,900	1.15
3	13	85	5,000	4,500	4,500	1.10
4	24	95	5,000	---	3,600	2.05
5	16	90	10,000	---	9,600	1.20

*PCL standards

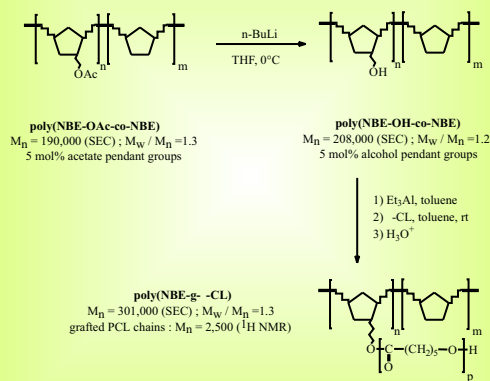
ROM-Copolymerization of PCL macromonomers



Macromonomer Code	X	Reaction Time (min)	Yield %	f _{cl}	F _{cl}	M _n * (SEC)	M _w /M _n
1	H	5	70	0.3	0.29	199,000	1.60
3	H	1	40	0.3	0.27	227,000	1.85
5	H	5	60	0.6	---	82,000	2.40
5	H	4	60	0.3	0.29	182,000	1.50
5	H	5	60	0.6	---	126,000	2.00
5	OAc	60	90	0.3	0.30	92,000	1.25
5	OAc	60	70	0.6	0.55	87,000	1.45

*Polystyrene standards

Synthesis of poly(NBE-g- ϵ -CL)



poly(NBE-OAc-co-NBE)
M_n = 190,000 (SEC); M_w / M_n = 1.3
5 mol% acetate pendant groups

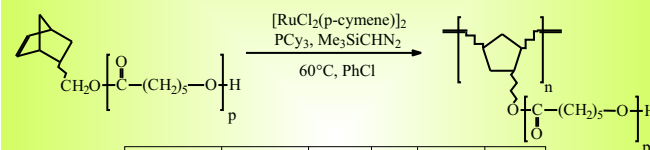
poly(NBE-OH-co-NBE)
M_n = 208,000 (SEC); M_w / M_n = 1.2
5 mol% alcohol pendant groups

poly(NBE-g- ϵ -CL)
M_n = 301,000 (SEC); M_w / M_n = 1.3
grafted PCL chains: M_n = 2,500 (¹H NMR)

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- 2) Demonceau, A.; Stumpf, A. W.; Saive, E.; Noels, A. *Macromolecules* 1997, 30, 3127.
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ROMP of PCL macromonomers



Macromonomer Code	[Macro] ₀ /[Ru] ₀	[Macro] ₀ (mol l ⁻¹)	Yield %	M _n * (SEC)	M _w /M _n
2	3	0.002	66	34,000	1.15
2	3	0.01	89	44,000	1.10
2	3	0.06	90	39,000	1.10
2	1.5	0.03	78	24,000	1.15
3	0.9	0.02	78	30,000	1.15
3	1.2	0.13	90	88,000	1.10

*Polystyrene standards

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