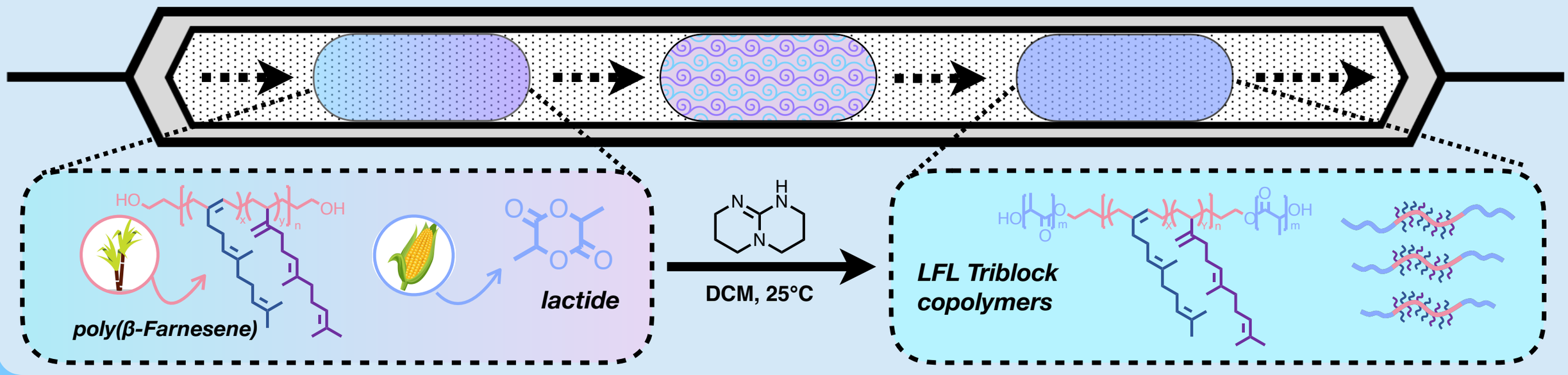
Investigating the depolymerisation kinetics of complex PLA-based block copolymers in a novel continuous flow set-up

Milan Den Haese[a], Louis M. Pitet[a]

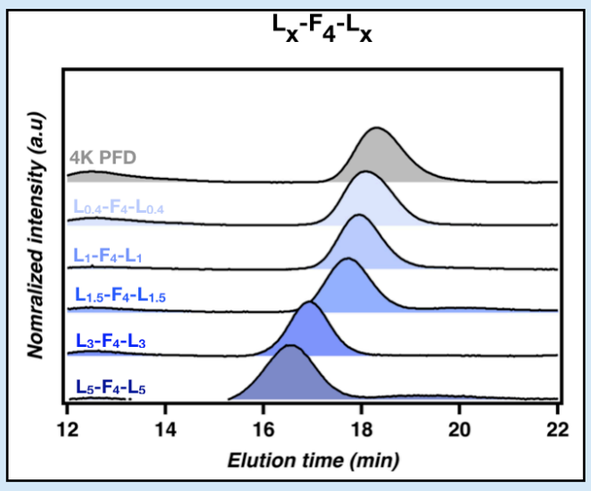
[a]Advanced Functional Polymers Laboratory, Institute for Materials Research (IMO), Hasselt University, Martelarenlaan 42, 3500 Hasselt, Belgium.

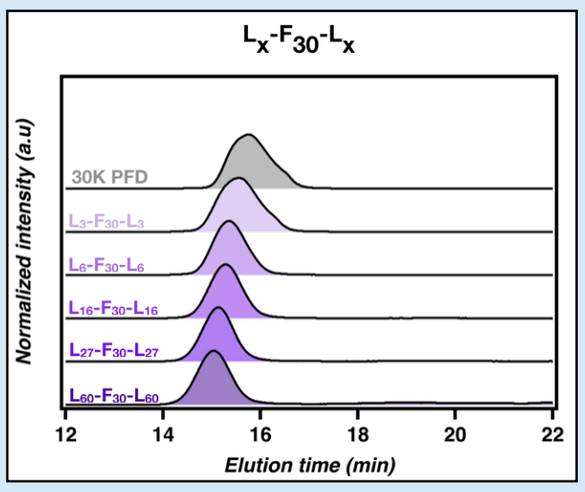
Block copolymer synthesis in new-generation flow reactor



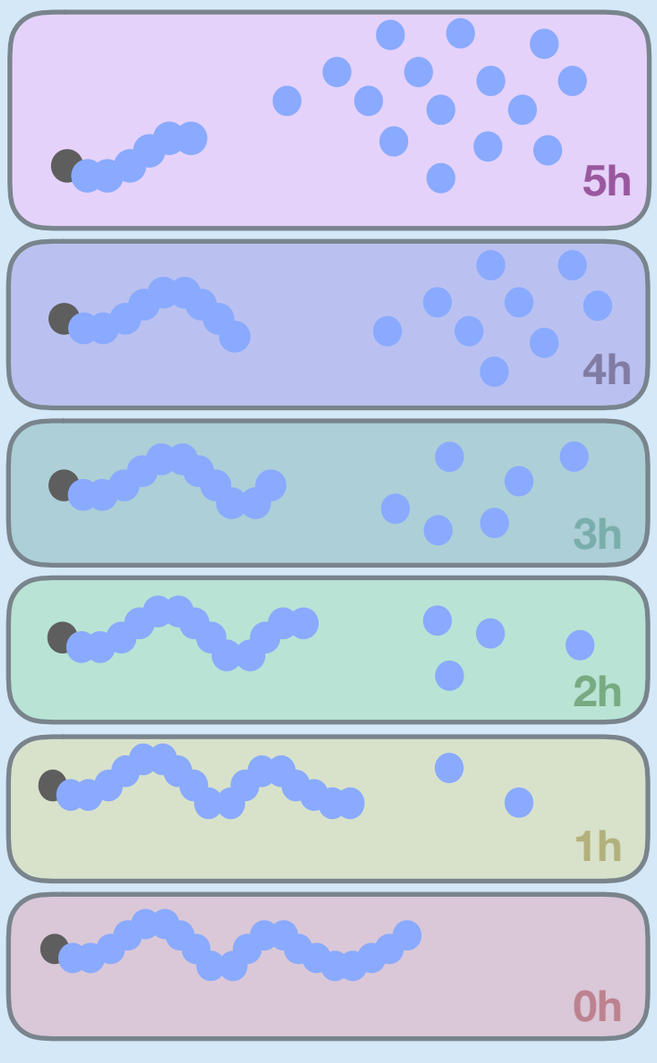
Block copolymer analysis

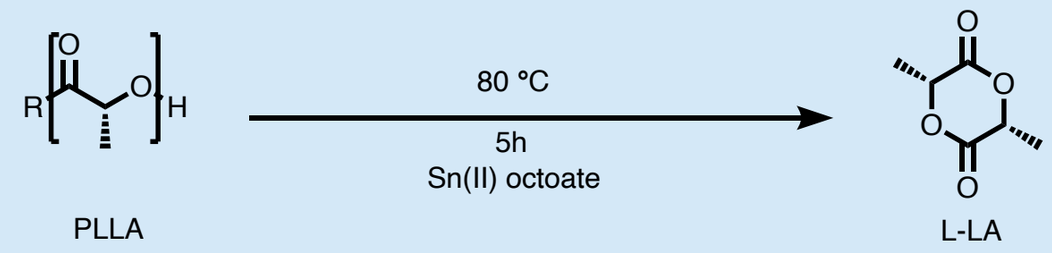
	Sample name	Target PLA composition (wt %)	M_w (kg/mol) (SEC)[a]	M_n (kg/mol) (SEC)[a]	ϕ_L (^{1}H NMR)[b]	ϕ_L (SEC)[c]	Đ[a]
PFD (4 kg/mol)	$L_{0.4}$-F_4-$L_{0.4}$	20	5.1	4.9	0.22	0.16	1.05
	L_1 -F_4-L_1	30	6.6	6.3	0.31	0.35	1.06
	$L_{1.5}$-F_4-$L_{1.5}$	50	7.2	7.0	0.52	0.41	1.03
	L_3-F_4-L_3	70	10.2	10.1	0.64	0.58	1.01
	L_5-F_4-L_5	80	13.6	13.6	0.76	0.69	1.00
PFD (30 kg/mol)	L_3-F_{30}-L_3	20	43.1	43.1	0.19	0.21	1.00
	L_6-F_{30}-L_6	30	47.7	47.7	0.34	0.28	1.00
	L_{16}-F_{30}-L_{16}	50	67.5	67.4	0.52	0.49	1.00
	L_{27}-F_{30}-L_{27}	70	90.4	89.4	0.73	0.62	1.01
	L_{60}-F_{30}-L_{60}	80	158.2	158	0.81	0.78	1.00

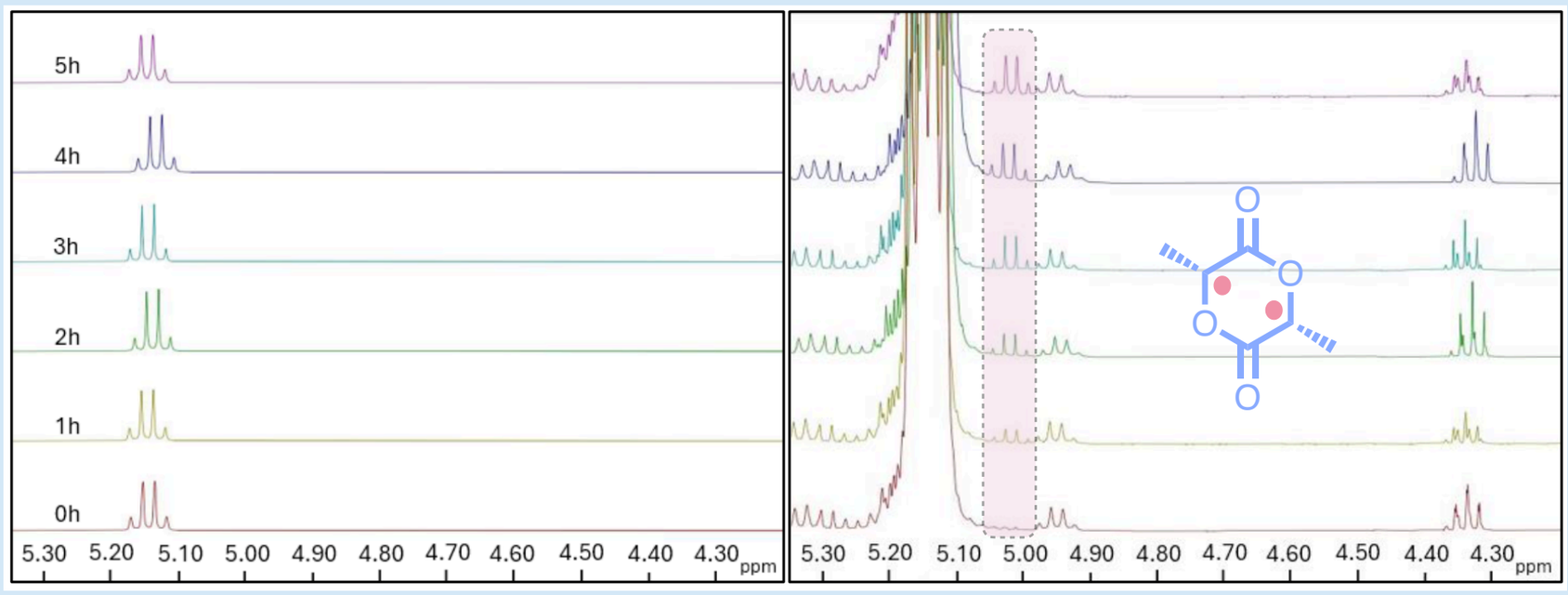




PLLA homopolymer depolymerization

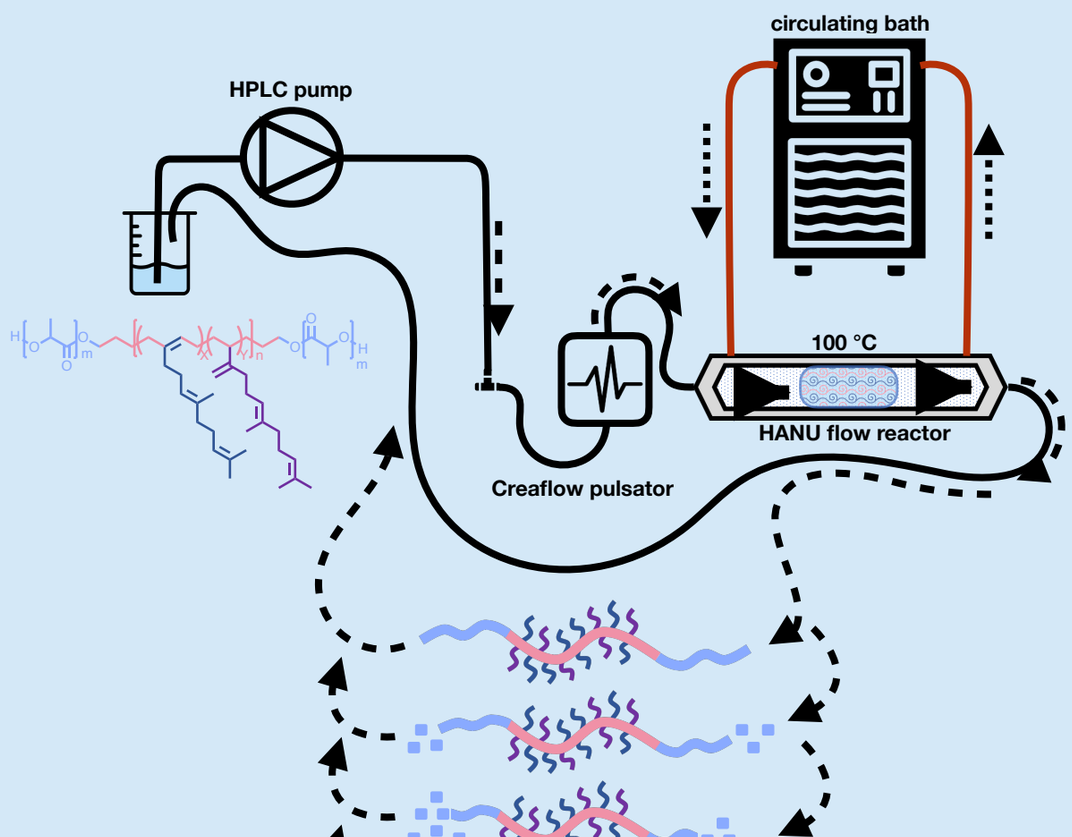




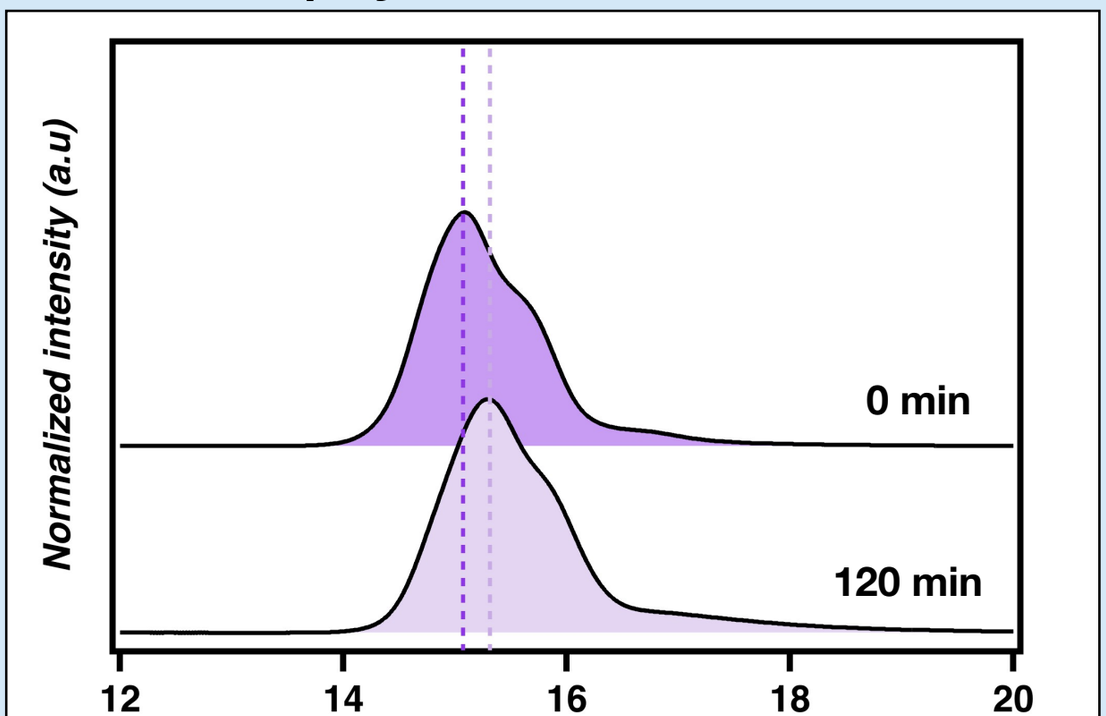


Systematically analysed aliquots of the reagent solution (1M PLLA) revealed the gradual increase of L-LA signal in 1H NMR spectroscopy. Numerous conditions were tested to find the optimal parameters such as catalyst concentration, PLLA concentration and temperature. However, due to these experiments being performed under batch conditions, there was a limit to the reaction temperature used. Literature suggests that temperature is one of the most prominent driving forces in pushing the reaction towards controlled depolymerization.

Block copolymer depolymerization



$L_{16}F_{30}L_{16}$ depolymerisation in continuous flow



Reaction time (min)	Peak position (mL)	Mw (kg/mol)	Mn (kg/mol)	Dispersity (Đ)
0	15.09	53.99	42.78	1.26
120	15.29	44.59	27.41	1.63

milan.denhaese@uhasselt.be
Universiteit Hasselt, Martelarenlaan 42, 3500 Hasselt, Belgium
www.louispitet.com
www.imo.uhasselt.com
www.creaflow.be

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