SUPPORTING INFORMATION

Polylactic Acid Macromonomer Radical Propagation Kinetics and Degradation Behaviour

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Macromonomer and Comb-Polymer Characterizations

Table S1: Characterization summary for PLA$_N$EMA (macro)monomer syntheses.

	LA conversion (%)	Yield (%)	*N*	
			Target	^{1}H NMR
PLA$_1$EMA	-	67	1	1
PLA$_5$EMA	94	77	5	5.3
PLA$_7$EMA	91	74	7	7.1
PLA$_9$EMA	97	62	9	9.5

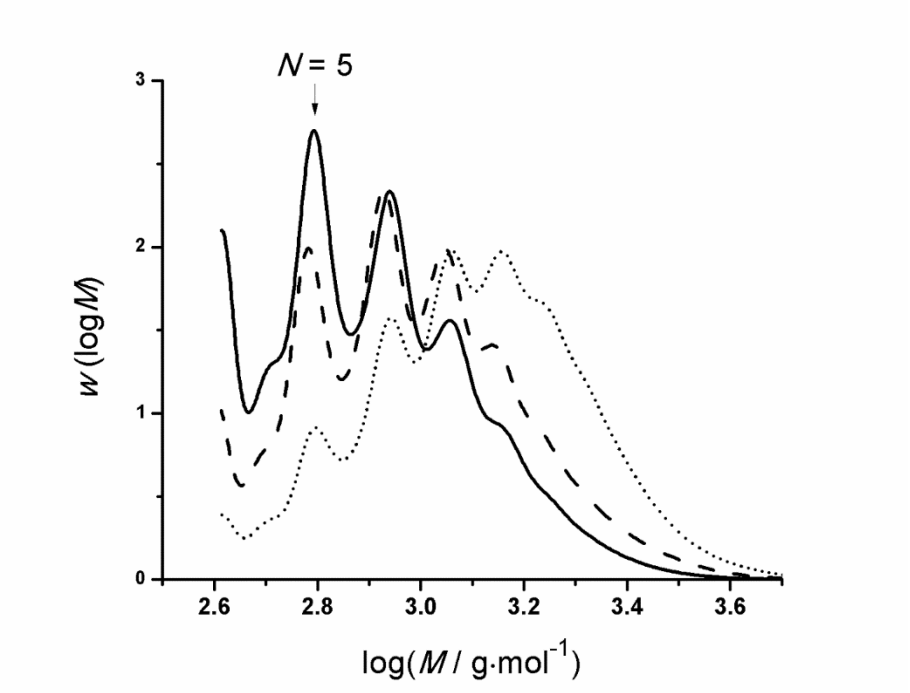

Figure S1: Molar mass distributions measured by size exclusion chromatography in THF and analyzed as polymethyl methacrylate equivalents for PLA_NEMA macromonomers N=5 (solid line), N=7 (dashed line), and N=9 (dotted line).

$$\left(\frac{1}{\rho_{mix}}\right) = \left(\frac{1}{\rho_{xylenes}}\right) + w_{PLA_NEMA} \cdot \left(\frac{1}{\rho_{PLA_NEMA}} - \frac{1}{\rho_{xylenes}}\right)$$

Table S2: Xylenes solution density measurements used to extrapolate density of PLA_5EMA assuming volume additivity.

	Weight fraction PLA_NEMA				
T (°C)	0.0	0.12	0.25	0.50	1.0 (extrapolated)
	ρ_{mix} (g·mL^{-1})				
25	0.8615	0.8896	0.9217	0.9908	1.165
50	0.8394	0.8677	0.8996	0.9680	1.142
70	0.8221	0.8495	0.8812	0.9491	1.122

Table S3: Xylenes solution density measurements used to extrapolate density of PLA_7EMA assuming volume additivity. 1.2198–0.000958·*T*/°C

	Weight fraction xylenes				
T (°C)	0.0	0.10	0.25	0.50	1.0 (extrapolated)
	ρ_{mix} ($g \cdot mL^{-1}$)				
25	0.8615	0.8849	0.9244	1.0006	1.196
50	0.8394	0.8632	0.9021	0.9777	1.184
70	0.8221	0.8451	0.8837	0.9588	1.165

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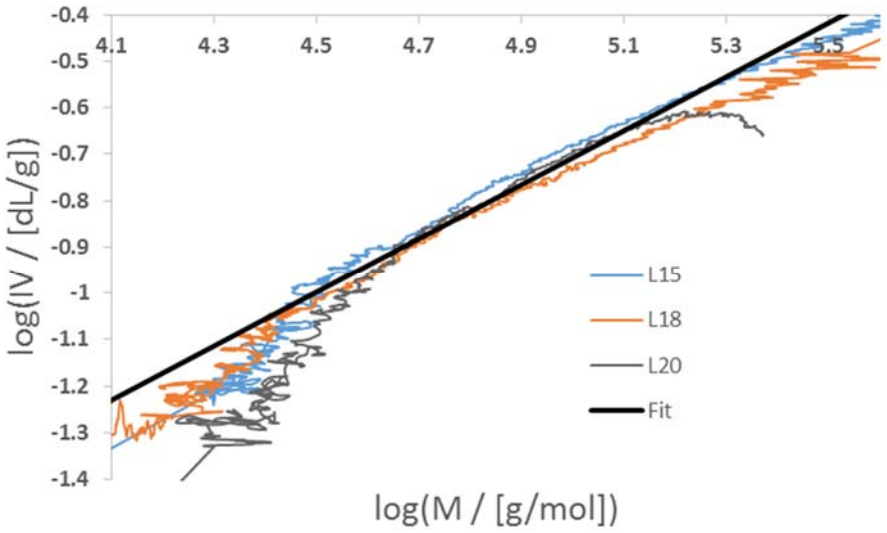

Figure S2: Mark-Houwink analysis for poly(PLA_1EMA). Fit performed by linear regression between log*M*=4.4 and log*M*=5.2 for three independent samples.

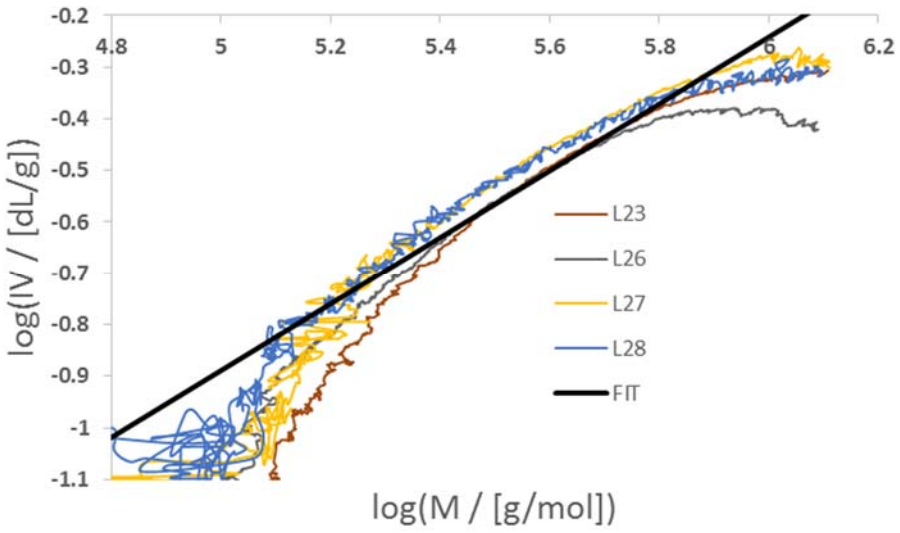

Figure S3: Mark-Houwink analysis for poly(PLA$_5$EMA). Fit performed by linear regression between log$M$=5.1 and log$M$=5.9 for four independent samples.

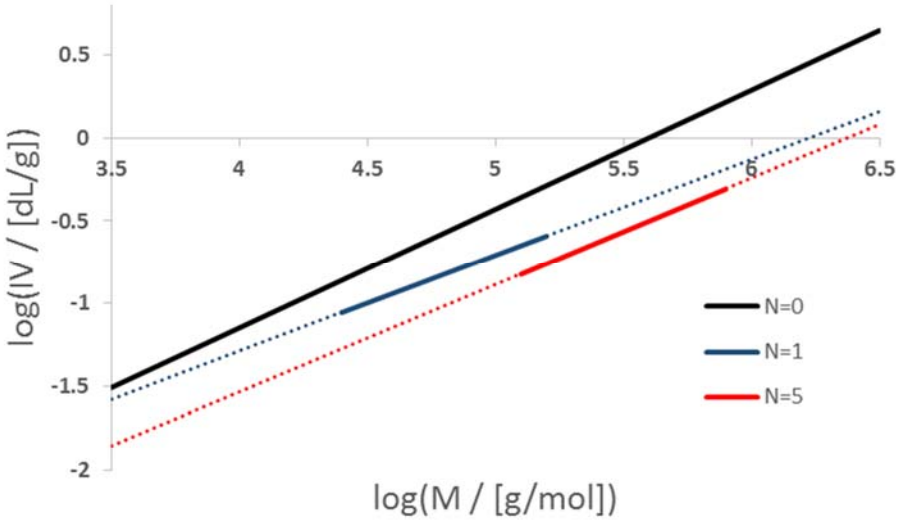

Figure S4: Intrinsic viscosity as a function of molecular weight for PMMA[1] (N=0), poly(PLA$_1$EMA), and poly(PLA$_5$EMA). The solid lines indicate fitted regions while the dotted lines represent extrapolations of the respective fits.

Pulsed Laser Polymerization Propagation Kinetics Study

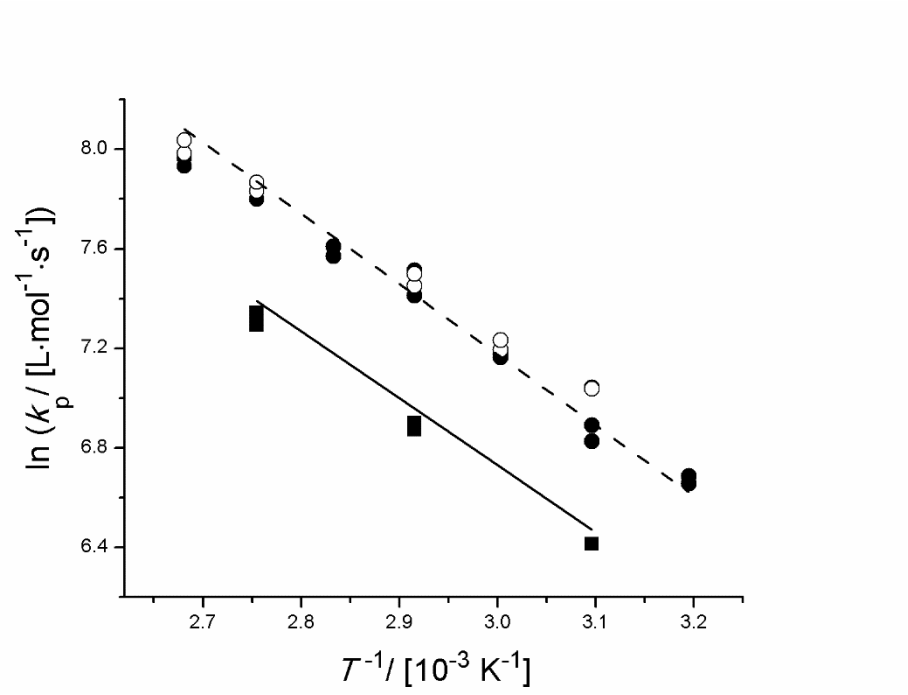

Figure S5: Arrhenius plot for k_p determined from bulk PLP experiments of MMA (■), PLA_1EMA (●), and PLA_5EMA (○) using universal calibration to interpret SEC output. The IUPAC benchmark MMA best fit line (solid)[1] is provided for comparison, while the N=1,5 data are fitted (dashed line) by a pre exponential of 6.5×10^6 L·mol^{-1}·s^{-1} using the MMA benchmark activation energy of 22.36 kJ·mol^{-1}.

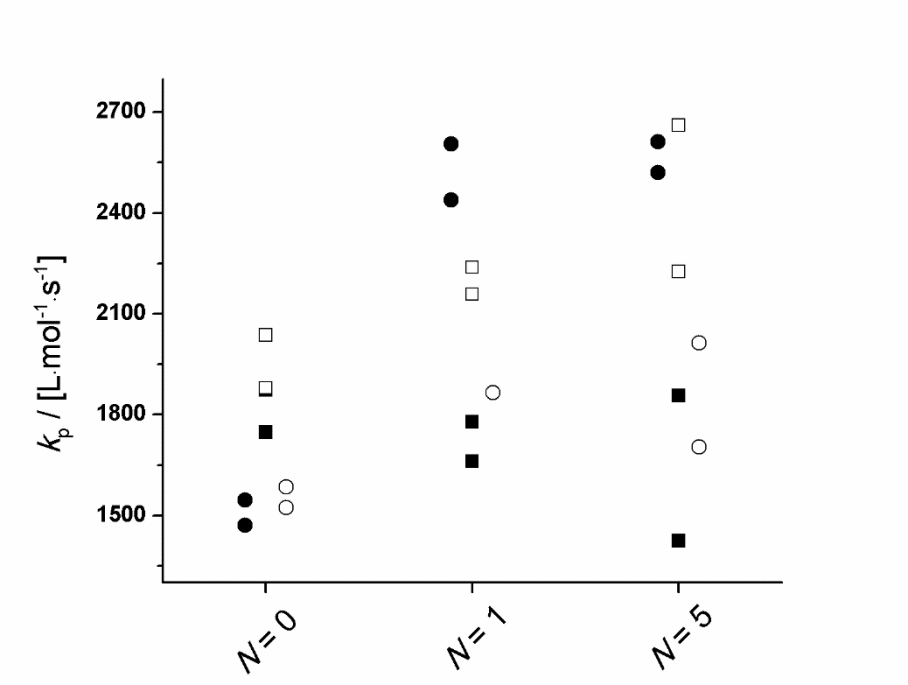

Figure S6: Plots for k_p of MMA, PLA$_1$EMA, and PLA$_5$EMA determined by universal calibration in bulk (●), 75 wt% xylenes (○), 75 wt% DMF (■), and 75 wt% BuOH (□) solutions at 90 °C with 5 mmol·L^{-1} DMPA.

Table S4: Ratio of k_p determined in BuOH to bulk/DMF at 90 °C with 5 mmol·L^{-1} DMPA at various δ for each (macro)monomer.

Monomer	δ	$\frac{k_{p,BuOH}}{k_{p,bulk}}$	$\frac{k_{p,BuOH}}{k_{p,DMF}}$
MMA	4.1	1.30	1.08
BMA[2]	5.3	1.26	-
	11.3	1.40	
PLA$_1$EMA	7.5	0.87	1.28
PLA$_5$EMA	19.1	0.95	1.49

Table S5: PLP conditions and results for MMA (N=0) homopolymerizations with [DMPA]=5 mmol·L^{-1} and 4.0 mJ/pulse.

T (°C)	Solvent (wt.%)	ϕ_{xMA}	[M] (mol·L^{-1})	Pulse Repetition Rate (Hz)	Pulse Time	Conv (%)	SEC Results						
							RI			LS			$k_{p,LS}/k_{p,RI}$
							M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	
50	Bulk	1	9.11	33	0:30	3.1	16,600	1.94	601	-	-	-	-
50	Bulk	1	9.11	50	0:17	1.9	11,100	1.96	610	10,500	1.88	579	0.95
50	75% Xyl	0.23	2.14	5	5:00	3.4	25,500	1.99	595	37,800	1.20	882	1.48
50	75% Xyl	0.23	2.14	10	3:00	4.7	13,600	1.95	636	18,100	1.69	844	1.33
70	Bulk	1	8.89	33	0:17	1.3	26,000	1.95	965	-	-	-	-
70	Bulk	1	8.89	50	0:14	2.8	17,700	1.95	993	-	-	-	-
70	43% BuOH	0.53	4.75	20	0:18	1.7	27,200	1.97	1146	36,100	2.02	1521	1.33
70	43% BuOH	0.53	4.75	33	0:15	1.4	17,300	1.95	1202	18,400	2.26	1278	1.06
70	75% DMF	0.25	2.25	5	4:00	5.7	49,400	2.02	1100	54,300	2.00	1209	1.10
70	75% DMF	0.25	2.25	10	3:00	6.2	26,600	1.97	1185	31,400	1.86	1398	1.18
70	75% BuOH	0.22	1.99	5	3:00	6.9	48,600	2.09	1221	58,800	1.33	1475	1.21
70	75% BuOH	0.22	1.99	10	2:00	4.7	26,600	2.00	1336	27,900	1.97	1402	1.05
70	75% Xyl	0.24	2.09	5	5:00	13.3	38,600	2.18	922	39800	1.85	950	1.03
70	75% Xyl	0.24	2.09	10	3:30	9.0	21,200	1.95	1011	22,100	1.81	1054	1.04
90	Bulk	1	8.67	33	0:18	1.8	38,600	2.00	1471	43,800	2.13	1666	1.13
90	Bulk	1	8.67	50	0:13	1.5	26,800	1.94	1546	24,900	2.21	1436	0.93
90	75% DMF	0.25	2.20	10	2:00	5.9	38,400	2.07	1747	43,400	1.94	1974	1.13
90	75% DMF	0.25	2.20	20	1:00	5.3	20,600	1.96	1873	22,300	2.02	2034	1.09
90	75% BuOH	0.22	1.95	10	2:00	6.3	36,600	2.06	1879	39,800	1.96	2044	1.09
90	75% BuOH	0.22	1.95	20	0:50	3.7	19,800	1.98	2036	19,300	2.24	1983	0.97
90	75% Xyl	0.24	2.05	10	2:00	4.4	31,200	2.08	1523	39,500	1.30	1926	1.27
90	75% Xyl	0.24	2.05	20	1:00	6.9	16,200	1.97	1584	18,100	1.50	1769	1.12

Table S6: PLP conditions for PLA_NEMA (N=1) bulk homopolymerizations with [DMPA]=5 mmol·L^{-1} and 3.5 mJ/pulse.

T (°C)	Solvent (wt.%)	ϕ_{xMA}	[M] (mol·L^{-1})	Pulse Repetition Rate (Hz)	Pulse Time	Conv (%)	SEC Results						
							RI			LS			
							M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	$k_{p,LS}/k_{p,RI}$
40	Bulk	1	5.40	33	0:40	1.8	23,700	2.02	777	25,700	1.83	843	1.09
40	Bulk	1	5.40	50	0:30	1.6	16,100	2.00	802	22,700	1.67	1128	1.41
50	Bulk	1	5.35	33			27,800	2.18	921	27,200	2.31	903	1.04
50	Bulk	1	5.35	50			19,600	2.02	983	18,400	2.14	925	0.94
60	Bulk	1	5.29	33	0:43	2.4	38,600	2.03	1292	41,100	1.83	1378	1.07
60	Bulk	1	5.29	50	0:33	1.8	25,800	2.02	1311	28,900	1.80	1468	1.12
70	Bulk	1	5.23	33			48,900	2.10	1656	-	-	-	-
70	Bulk	1	5.23	50			33,900	1.96	1832	-	-	-	-
80	Bulk	1	5.18	33	0:33	2.0	56,600	2.12	1939	62,200	1.72	2130	1.10
80	Bulk	1	5.18	50	0:22	2.0	38,900	2.05	2016	48,000	1.63	2488	1.23
90	Bulk	1	5.12	33			70,500	2.20	2439	-	-	-	-
90	Bulk	1	5.12	50			49,700	2.10	2606	-	-	-	-
100	Bulk	1	5.06	33	0:36	2.9	79,500	2.05	2784	90,800	1.61	3177	1.14
100	Bulk	1	5.06	50	0:26	2.7	54,300	2.11	2877	56,000	1.91	2968	1.03

Table S7: PLP conditions for PLA_NEMA (N=1) solution homopolymerizations with [DMPA]=5 mmol·L^{-1} and 4.0 mJ/pulse.

T (°C)	Solvent (wt.%)	ϕ_{xMA}	[M] (mol·L^{-1})	Pulse Repetition Rate (Hz)	Pulse Time	Conv (%)	SEC Results						
							RI			LS			$k_{p,LS}/k_{p,RI}$
							M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	
70	Bulk	1	5.23	33			48,900	2.10	1656	-	-	-	-
70	Bulk	1	5.23	50			33,900	1.96	1832	-	-	-	-
70	28% BuOH	0.67	3.51	20	0:45	1.7	44,700	2.27	1369	50,800	1.81	1556	1.14
70	28% BuOH	0.67	3.51	33	0:50	2.0	29,100	2.05	1469	29,200	1.74	1474	1.00
70	75% DMF	0.24	1.23	5	3:00	1.0	49,900	2.43	1318	48,600	1.81	1123	0.98
70	75% DMF	0.24	1.23	10	2:00	0.9	27,100	2.18	1179	-	-	-	-
70	75% BuOH	0.21	1.09	5	2:30	-	62,200	2.35	1531	57,300	1.81	1409	0.92
70	75% BuOH	0.21	1.09	10	2:00	1.4	32,800	2.13	1613	-	-	-	-
70	75% Xyl	0.22	1.15	5	3:00	0.3	20,300	-	-	-	-	-	-
70	75% Xyl	0.22	1.15	10	2:00	0.4	26,400	2.26	1236	-	-	-	-
90	Bulk	1	5.12	33			70,500	2.20	2439	-	-	-	-
90	Bulk	1	5.12	50			49,700	2.10	2606	-	-	-	-
90	75% DMF	0.24	1.21	10	2:00	0.9	37,300	2.37	1660	46,000	1.66	2047	1.23
90	75% DMF	0.24	1.21	20	1:00	0.9	20,000	2.06	1777	-	-	-	-
90	75% BuOH	0.21	1.07	10	2:00	1.8	42,900	2.24	2158	41,100	2.05	2067	0.96
90	75% BuOH	0.21	1.07	20	1:00	1.6	22,300	2.08	2238	22,200	1.89	2236	1.00
90	75% Xyl	0.22	1.12	10	2:00	0.9	19,400	-	-	-	-	-	-
90	75% Xyl	0.22	1.12	20	0:50	0.6	19,500	2.12	1865	-	-	-	-

Table S8: PLP conditions for PLA_NEMA (N=5) bulk homopolymerizations with [DMPA]=5 mmol·L^{-1} and 2.5 mJ/pulse. Italicised data not used in Arrhenius fitting or any further analyses.

T (℃)	Solvent (wt.%)	ϕ_{xMA}	[M] (mol·L^{-1})	Pulse Repetition Rate (Hz)	Pulse #	Conv (%)	SEC Results						
							RI			LS			
							M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	$k_{p,LS}/k_{p,RI}$
50	Bulk	1	2.41	10	100	4.5	130,700	1.60	1145	142,200	1.64	1246	1.09
50	Bulk	1	2.41	20	100	3.7	65,000	2.14	1139	53,600	3.05	939	0.83
60	Bulk	1	2.39	10	100	2.3	150,600	1.77	1331	162,600	1.91	1436	1.08
60	Bulk	1	2.39	20	100	3.5	78,400	1.99	1385	71,600	2.29	1265	0.91
70	*Bulk*	*1*	*2.37*	*10*	*100*	*4.2*	*175,800*	*1.71*	*1336*	*220,800*	*1.88*	*1967*	*1.26*
70	Bulk	1	2.37	20	100	3.1	96,600	1.85	1721	107,200	2.06	1909	1.11
70	Bulk	1	2.37	33	100	2.8	61,400	2.04	1806	55,200	2.61	1623	0.90
90	*Bulk*	*1*	*2.33*	*10*	*100*	*2.8*	*232,800*	*1.98*	*2110*	*276,700*	*1.95*	*2508*	*1.19*
90	Bulk	1	2.33	20	100	2.2	139,900	1.77	2520	164,100	1.81	2974	1.18
90	Bulk	1	2.33	33	100	1.8	87,300	1.91	2612	99,500	2.07	2978	1.14
100	Bulk	1	2.31	20	100	2.0	160,500	1.85	2934	179,500	1.92	3149	1.12
100	Bulk	1	2.31	33	100	1.5	102,500	1.85	3093	105,000	2.01	3167	1.02

Table S9: PLP conditions for PLA_NEMA (N=5) solution homopolymerizations with [DMPA]=5 mmol·L^{-1} and 3.0 mJ/pulse.

T (°C)	Solvent (wt.%)	ϕ_{xMA}	[M] (mol·L^{-1})	Pulse Repetition Rate (Hz)	Pulse Time	Conv (%)	SEC Results						
							RI			LS			$k_{p,LS}/k_{p,RI}$
							M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	M_1 (g·mol^{-1})	M_2/M_1	k_p from M_1 (L·mol^{-1}·s^{-1})	
70	Bulk	1	2.37	20	0:05	3.1	96,600	1.85	1721	107,200	2.06	1909	1.11
70	Bulk	1	2.37	33	0:03	2.8	61,400	2.04	1806	55,200	2.61	1623	0.90
70	75% DMF	0.21	0.50	5	3:30	3.6	45,500	1.90	961	40,000	2.05	844	0.88
70	75% DMF	0.21	0.50	10	2:15	2.2	27,200	1.78	1149	23,400	1.88	989	0.86
70	75% BuOH	0.19	0.44	5	3:30	2.7	73,400	2.05	1757	70,300	2.05	1683	0.96
70	75% BuOH	0.19	0.44	10	2:15	3.1	42,200	1.88	2018	36,700	1.97	1758	0.87
70	75% Xyl	0.20	0.46	5	3:30	7.3	46,200	1.94	1050	43,100	1.95	977	0.93
70	75% Xyl	0.20	0.46	10	2:30	5.6	29,100	1.75	1322	28,000	1.70	1271	0.96
90	Bulk	1	2.33	20	0:05	2.2	139,900	1.77	2520	164,100	1.81	2974	1.18
90	Bulk	1	2.33	33	0:03	1.8	87,300	1.91	2612	99,500	2.07	2978	1.14
90	75% DMF	0.21	0.49	10	2:00	2.7	33,100	1.73	1424	27,700	1.87	1182	0.84
90	75% DMF	0.21	0.49	20	1:00	2.1	21,600	1.68	1856	17,900	1.79	1539	0.83
90	75% BuOH	0.19	0.43	10	2:00	3.7	45,500	1.93	2225	39,100	2.09	1910	0.86
90	75% BuOH	0.19	0.43	20	1:00	2.7	27,200	1.79	2661	22,200	1.91	2168	0.86
90	75% Xyl	0.20	0.46	10	2:00	2.0	36,700	1.80	1703	31,100	1.82	1439	0.85
90	75% Xyl	0.20	0.46	20	1:00	1.6	21,700	1.80	2013	22,500	1.77	2085	1.04

Nanoparticle Degradation

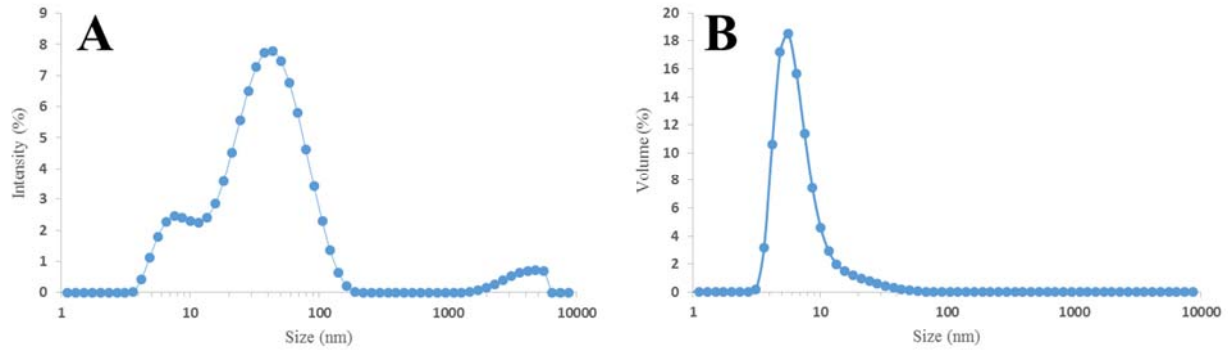

Figure S7: Intensity (A) and volume (B) particle size distributions measured at 25 °C on day 0 of the accelerated degradation study of the 5 wt% latex produced from PLA_1EMA with 1% SDS as surfactant.

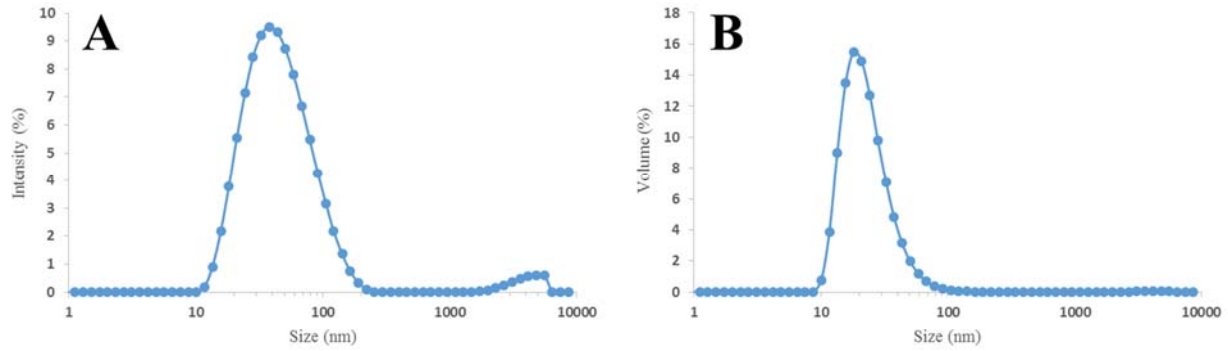

Figure S8: Intensity (A) and volume (B) particle size distributions measured at 25 °C on day 0 of the accelerated degradation study of the 5 wt% latex produced from PLA_5EMA with 1% SDS as surfactant.

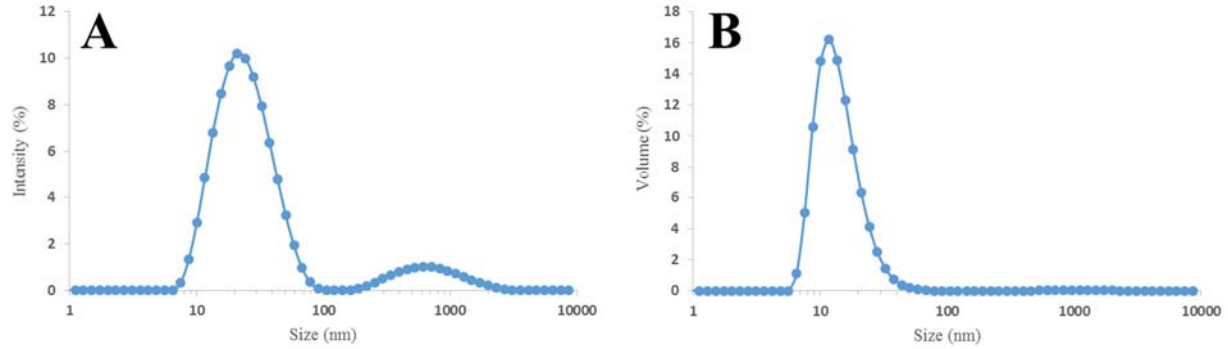

Figure S9: Intensity (A) and volume (B) particle size distributions measured at 25 °C on day 0 of the accelerated degradation study of the 5 wt% latex produced from an equal mass macromonomer mixture of PLA_5EMA and $HEMA\text{-}PLA_5$ with 1% SDS as surfactant.

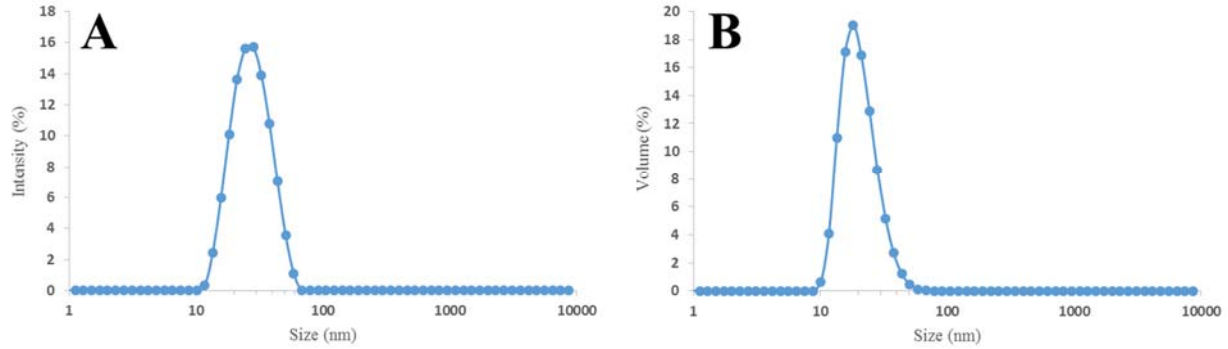

Figure S10: Intensity (A) and volume (B) particle size distributions measured at 25 °C on day 0 of the accelerated degradation study of the 5 wt% latex produced from $HEMA\text{-}PLA_5$ with 1% SDS as surfactant.

Table S10: *pH* measurements of latex taken at room temperature throughout the accelerated NP degradation study performed at 50 °C.

Degradation Time (days)	*pH* of 5 wt% latex	
	PLA_1EMA	PLA_5EMA
0	6.8	6.4
34.5	2.8	2.1

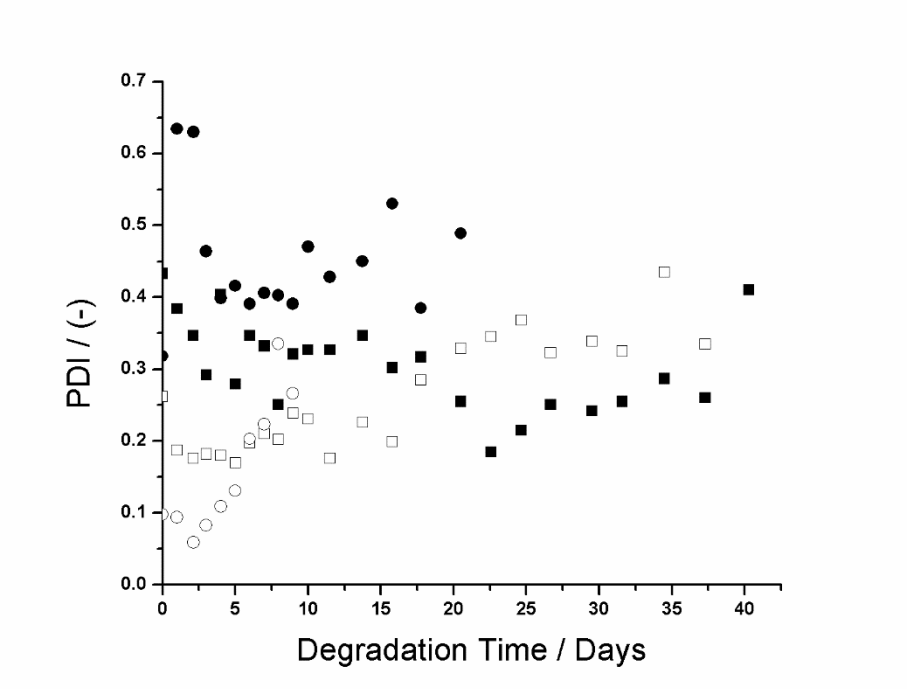

Figure S11: Polydispersity indices (PDI) measured at 25 °C for NPs produced from PLA_1EMA (■), PLA_5EMA (□), an equal mass copolymer of PLA_5EMA and HEMA-PLA_5 (●), and HEMA-PLA_5 (○) throughout the accelerated degradation study at 50 °C.

References

(1) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. A.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545.
(2) Beuermann, S. *Macromolecules* **2004**, *37*, 1037.