Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to

Pulsed Laser Polymerization – Size Exclusion Chromatography Investigations into Backbiting in Ethylhexyl Acrylate Polymerization

Greg Quintens,[a] *Tanja Junkers*[b*]

[a]Universiteit Hasselt, Martelarenlaan 42, 3500 Hasselt, Belgium

[b]Polymer Reaction Design Group, Monash University, 19 Rainforest Walk, Clayton VIC 3800, Australia, email: tanja.junkers@monash.edu

All primary results from PLP experiments on EHA are collated in the supporting information section. Density function and Mark-Houwing-Kuhn-Sakurada parameters are taken from:

T. Junkers, M. Schneider-Baumann, S.P.S. Koo, P. Castignolles, and C. Barner-Kowollik, *Macromolecules* **2010**, *43*, 10427-10434.

Table S1 Experimental details showing frequency (*f*), number of pulses (*n*), monomer density (ρ), monomer concentration (C_M), the molecular weight at the inflection points (M_1 and M_2) and the calculated propagation constant ($k_p^{apparant}$) at 5° C

f / Hz	n	ρ / g·mL^{-1}	C_M / mol·L^{-1}	M_1 / g·mol^{-1}	M_2 / g·mol^{-1}	$k_p^{apparant}$ / L·mol^{-1}·s^{-1}
10	50	0.89722	4.8688	226049		2519
10	100	0.89722	4.8688	226354		2523
10	150	0.89722	4.8688	350998		3912
20	100	0.89722	4.8688	194083		4326
20	300	0.89722	4.8688	214723		4786
30	150	0.89722	4.8688	133044		4449
30	200	0.89722	4.8688	147288		4925
30	300	0.89722	4.8688	137306		4591
40	250	0.89722	4.8688	100502		4481
40	350	0.89722	4.8688	100233		4469
50	150	0.89722	4.8688	101158		5637
50	250	0.89722	4.8688	108705		6058
50	350	0.89722	4.8688	106232		5920
60	200	0.89722	4.8688	107978		7221
60	300	0.89722	4.8688	100400		6714
60	400	0.89722	4.8688	100027		6689
70	200	0.89722	4.8688	96414		7522
70	300	0.89722	4.8688	99555		7767
70	400	0.89722	4.8688	100066		7807
80	200	0.89722	4.8688	87198		7775
80	300	0.89722	4.8688	87807		7829
80	400	0.89722	4.8688	83107		7410
90	200	0.89722	4.8688	80541		8079
90	300	0.89722	4.8688	75812		7605
90	400	0.89722	4.8688	71550		7177
100	250	0.89722	4.8688	66361		7396
100	350	0.89722	4.8688	70902		7902
100	500	0.89722	4.8688	73741		8219
200	250	0.89722	4.8688	37557	78575	8372
200	350	0.89722	4.8688	38799	80180	8649
200	500	0.89722	4.8688	39313	78432	8763
300	300	0.89722	4.8688	27887	55138	9324
300	400	0.89722	4.8688	27460	55585	9182
300	500	0.89722	4.8688	28661	58632	9583
400	350	0.89722	4.8688	20971	42346	9349
400	500	0.89722	4.8688	21685	43688	9668
400	750	0.89722	4.8688	21862	44014	9747
500	350	0.89722	4.8688	16461	33830	9173
500	500	0.89722	4.8688	16598	35284	9249
500	750	0.89722	4.8688	17500	38056	9752
600	500	0.89722	4.8688	14485	30555	9686
600	750	0.89722	4.8688	15166	31991	10141
600	1000	0.89722	4.8688	15767	32413	10543
700	500	0.89722	4.8688	12892	26173	10058
700	750	0.89722	4.8688	13515	28093	10544
700	1000	0.89722	4.8688	14147	29652	11037
800	500	0.89722	4.8688	11363	23855	10132
800	750	0.89722	4.8688	12308	25969	10974
800	1000	0.89722	4.8688	12330	26645	10994
900	500	0.89722	4.8688	10747	21242	10780
900	750	0.89722	4.8688	11486	23028	11522
900	1000	0.89722	4.8688	12304	27367	12342
1000	350	0.89722	4.8688	9548	18813	10642
1000	500	0.89722	4.8688	9401	18578	10478
1000	750	0.89722	4.8688	10620	21269	11837
1000	1000	0.89722	4.8688	10566	22547	11776

Table S2 Experimental details showing frequency (f), number of pulses (n), monomer density (ρ), monomer concentration (C_M), the molecular weight at the inflection points (M_1 and M_2) and the calculated propagation constant ($k_p^{apparant}$) at 20° C

f / Hz	n	ρ / g·mL^{-1}	C_M / mol·L^{-1}	M_1 / g·mol^{-1}	M_2 / g·mol^{-1}	$k_p^{apparant}$ / L·mol^{-1}·s^{-1}
1	25	0.88481	4.8015	1578210		1784
5	50	0.88481	4.8015	315032		1780
10	50	0.88481	4.8015	111763		1263
10	100	0.88481	4.8015	117111		1324
10	150	0.88481	4.8015	108074		1221
20	100	0.88481	4.8015	101401		2292
20	200	0.88481	4.8015	95308		2154
30	100	0.88481	4.8015	93537		3171
30	150	0.88481	4.8015	93913		3184
30	200	0.88481	4.8015	95759		3247
40	100	0.88481	4.8015	77191		3490
40	150	0.88481	4.8015	77141		3487
40	200	0.88481	4.8015	82425		3726
50	100	0.88481	4.8015	68862		3891
50	150	0.88481	4.8015	67588		3819
50	200	0.88481	4.8015	71068		4016
60	150	0.88481	4.8015	78718		5338
60	200	0.88481	4.8015	72765		4934
70	150	0.88481	4.8015	87497		6922
70	200	0.88481	4.8015	81722		6465
70	250	0.88481	4.8015	75349		5961
80	250	0.88481	4.8015	57259		5177
90	150	0.88481	4.8015	63844		6494
90	200	0.88481	4.8015	60501		6154
90	250	0.88481	4.8015	75014		7630
100	200	0.88481	4.8015	70494		7967
100	250	0.88481	4.8015	68491		7741
200	150	0.88481	4.8015	37998		8589
200	200	0.88481	4.8015	40268		9102
200	250	0.88481	4.8015	42779		9670
300	200	0.88481	4.8015	33354	68795	11309
300	250	0.88481	4.8015	34189	67084	11592
300	300	0.88481	4.8015	35174	70217	11926
400	250	0.88481	4.8015	28492	54387	12881
400	350	0.88481	4.8015	28491	53578	12880
400	500	0.88481	4.8015	28550	53147	12907
500	350	0.88481	4.8015	23974	45366	13548
500	500	0.88481	4.8015	24512		13852
500	750	0.88481	4.8015	27872		15750
600	350	0.88481	4.8015	18052	38690	12241
600	500	0.88481	4.8015	20192	36094	13692
700	350	0.88481	4.8015	16481	33967	13038
700	500	0.88481	4.8015	16434	32695	13001
700	750	0.88481	4.8015	17067	29719	13502
800	350	0.88481	4.8015	14148	30362	12792
800	500	0.88481	4.8015	15881	30918	14359
800	750	0.88481	4.8015	16139	28516	14592
900	350	0.88481	4.8015	13048	27073	13272
900	500	0.88481	4.8015	13329	28528	13558
900	750	0.88481	4.8015	13895	28227	14134
1000	350	0.88481	4.8015	12219	25429	13810
1000	500	0.88481	4.8015	11757	26706	13288
1000	750	0.88481	4.8015	13552	26316	15316
1000	1000	0.88481	4.8015	15611	28535	17643

Table S3 Experimental details showing frequency (*f*), number of pulses (*n*), monomer density (ρ), monomer concentration (C_M), the molecular weight at the inflection points (M_1 and M_2) and the calculated propagation constant ($k_p^{apparant}$) at 30° C

f / (Hz)	n	ρ / g·mL^{-1}	C_M / mol·L^{-1}	M_1 / g·mol^{-1}	M_2 / g·mol^{-1}	$k_p^{apparant}$/ L·mol^{-1}·s^{-1}
10	100	0.87662	4.7571	579206		6607
20	200	0.87662	4.7571	290860		6637
60	100	0.87662	4.7571	115920		7934
60	150	0.87662	4.7571	136126		9317
60	200	0.87662	4.7571	122589		8391
80	150	0.87662	4.7571	118492		10813
100	150	0.87662	4.7571	126286		14406
100	200	0.87662	4.7571	115628		13190
100	250	0.87662	4.7571	121971		13914
200	150	0.87662	4.7571	64321	123621	14675
200	200	0.87662	4.7571	63138	121261	14405
200	250	0.87662	4.7571	65813	126111	15015
300	200	0.87662	4.7571	43937	86628	15036
300	250	0.87662	4.7571	45263	89670	15490
300	300	0.87662	4.7571	44060	86900	15078
400	250	0.87662	4.7571	34111	66714	15565
400	350	0.87662	4.7571	34913	65807	15931
400	500	0.87662	4.7571	35723	67249	16300
500	350	0.87662	4.7571	28481	53706	16245
500	500	0.87662	4.7571	29264	55728	16691
500	750	0.87662	4.7571	29277		16699
600	350	0.87662	4.7571	25240	46283	17275
600	500	0.87662	4.7571	25283	48988	17305
600	750	0.87662	4.7571	25215	47520	17258
700	350	0.87662	4.7571	21215	39647	16941
700	500	0.87662	4.7571	20964	40721	16740
700	750	0.87662	4.7571	21765	40635	17380
800	350	0.87662	4.7571	19236	36588	17555
800	500	0.87662	4.7571	19394	36591	17699
800	750	0.87662	4.7571	19528	37841	17821
900	350	0.87662	4.7571	16967	32945	17419
900	500	0.87662	4.7571	17583	32539	18052
900	750	0.87662	4.7571	19132	37342	19642
1000	350	0.87662	4.7571	16932	32737	19315
1000	500	0.87662	4.7571	16037	31615	18294
1000	750	0.87662	4.7571	16964	34363	19351
1000	1000	0.87662	4.7571	16359	32992	18661

Table S4 Experimental details showing frequency (f), number of pulses (n), monomer density (ρ), monomer concentration (C_M), the molecular weight at the inflection points (M_1 and M_2) and the calculated propagation constant ($k_p^{apparant}$) at 40° C

f / Hz	n	ρ / g·mL^{-1}	C_M /mol·L^{-1}	M_1 / g·mol^{-1}	M_2 / g·mol^{-1}	$k_p^{apparant}$/ L·mol^{-1}·s^{-1}
1	12	0.86852	4.7131	249724		288
5	25	0.86852	4.7131	189877		1093
10	50	0.86852	4.7131	164990		1900
20	50	0.86852	4.7131	127103		2927
30	100	0.86852	4.7131	99140		3424
30	150	0.86852	4.7131	109663		3788
30	200	0.86852	4.7131	114194		3944
40	100	0.86852	4.7131	85998		3961
40	150	0.86852	4.7131	108426		4994
40	200	0.86852	4.7131	101190		4660
50	100	0.86852	4.7131	92669		5335
50	150	0.86852	4.7131	93557		5386
50	200	0.86852	4.7131	103076		5934
60	150	0.86852	4.7131	97345		6725
60	200	0.86852	4.7131	90939		6282
60	250	0.86852	4.7131	86597		5982
70	150	0.86852	4.7131	78934		6362
70	200	0.86852	4.7131	83740		6749
70	250	0.86852	4.7131	80671		6502
80	150	0.86852	4.7131	77346		7124
80	200	0.86852	4.7131	76569		7053
80	250	0.86852	4.7131	99899		9202
90	200	0.86852	4.7131	86993		9015
90	250	0.86852	4.7131	93172		9655
100	150	0.86852	4.7131	72877		8391
100	200	0.86852	4.7131	66375		7642
100	250	0.86852	4.7131	63865		7353
200	150	0.86852	4.7131	54572		12567
200	250	0.86852	4.7131	52141		12007
300	200	0.86852	4.7131	45541		15731
300	250	0.86852	4.7131	43737		15107
300	300	0.86852	4.7131	43948		15180
400	250	0.86852	4.7131	39801		18331
400	350	0.86852	4.7131	36364		16748
400	500	0.86852	4.7131	38749		17846
500	350	0.86852	4.7131	33014		19006
500	500	0.86852	4.7131	35157		20240
600	350	0.86852	4.7131	28629		19778
600	500	0.86852	4.7131	29574		20431
700	350	0.86852	4.7131	25116	43820	20243
700	500	0.86852	4.7131	25684		20701
800	350	0.86852	4.7131	22115	42292	20370
800	750	0.86852	4.7131	25818		23781
900	350	0.86852	4.7131	19134	38887	19828
900	500	0.86852	4.7131	21482	42645	22260
900	750	0.86852	4.7131	24024	39719	24895
1000	350	0.86852	4.7131	19116	39719	22010
1000	750	0.86852	4.7131	20259	37921	23326
1000	1000	0.86852	4.7131	22103	38171	25449

Table S5 Experimental details showing frequency (f), number of pulses (n), monomer density (ρ), monomer concentration (C_M), the molecular weight at the inflection points (M_1 and M_2) and the calculated propagation constant ($k_p^{apparant}$) at 50° C

f / Hz	n	ρ / g·mL^{-1}	C_M /mol·L^{-1}	M_1 / g·mol^{-1}	M_2 / g·mol^{-1}	$k_p^{apparant}$/ L·mol^{-1}·s^{-1}
400	200	0.86049	4.6695	47788	91942	22214
400	300	0.86049	4.6695	47847	86365	22242
400	500	0.86049	4.6695	47123		21905
500	250	0.86049	4.6695	36995	74062	21497
500	350	0.86049	4.6695	39866	76714	23165
500	500	0.86049	4.6695	38480		22359
600	350	0.86049	4.6695	34489	62612	24048
600	500	0.86049	4.6695	34224		23864
600	650	0.86049	4.6695	35386		24674
700	350	0.86049	4.6695	30506	56962	24816
700	500	0.86049	4.6695	30151	56297	24528
700	650	0.86049	4.6695	30847		25094
800	350	0.86049	4.6695	27046	51026	25144
800	500	0.86049	4.6695	27350	51100	25427
800	650	0.86049	4.6695	26705	48352	24828
900	350	0.86049	4.6695	23638	46017	24723
900	500	0.86049	4.6695	25133	45976	26287
900	650	0.86049	4.6695	25631	48779	26808
1000	350	0.86049	4.6695	23214	45439	26978
1000	500	0.86049	4.6695	23625	42744	27455
1000	650	0.86049	4.6695	24820	45266	28844
1000	800	0.86049	4.6695	25206	46388	29293

Table S6 Experimental details showing frequency (f), number of pulses (n), monomer density (ρ), monomer concentration (C_M), the molecular weight at the inflection points (M_1 and M_2) and the calculated propagation constant ($k_p^{apparant}$) at 60° C

f / Hz	n	ρ / g·mL^{-1}	C_M / mol·L^{-1}	M_1 / g·mol^{-1}	M_2 / g·mol^{-1}	$k_p^{apparant}$/ L·mol^{-1}·s^{-1}
80	200	0.85253	4.6263	111334		10447
500	350	0.85253	4.6263	42068		24672
500	500	0.85253	4.6263	39448		23136
600	350	0.85253	4.6263	37308		26257
600	500	0.85253	4.6263	39309		27665
600	650	0.85253	4.6263	34997		24630
700	350	0.85253	4.6263	37541		30824
800	350	0.85253	4.6263	31519		29577
800	500	0.85253	4.6263	35253		33081
800	650	0.85253	4.6263	33492		31428
900	350	0.85253	4.6263	29505	54502	31148
900	500	0.85253	4.6263	30188	52887	31869
900	650	0.85253	4.6263	30129		31087
1000	350	0.85253	4.6263	27058	51671	31738
1000	500	0.85253	4.6263	27279	49661	31998
1000	650	0.85253	4.6263	28139	49509	33006
1000	800	0.85253	4.6263	27522		32283

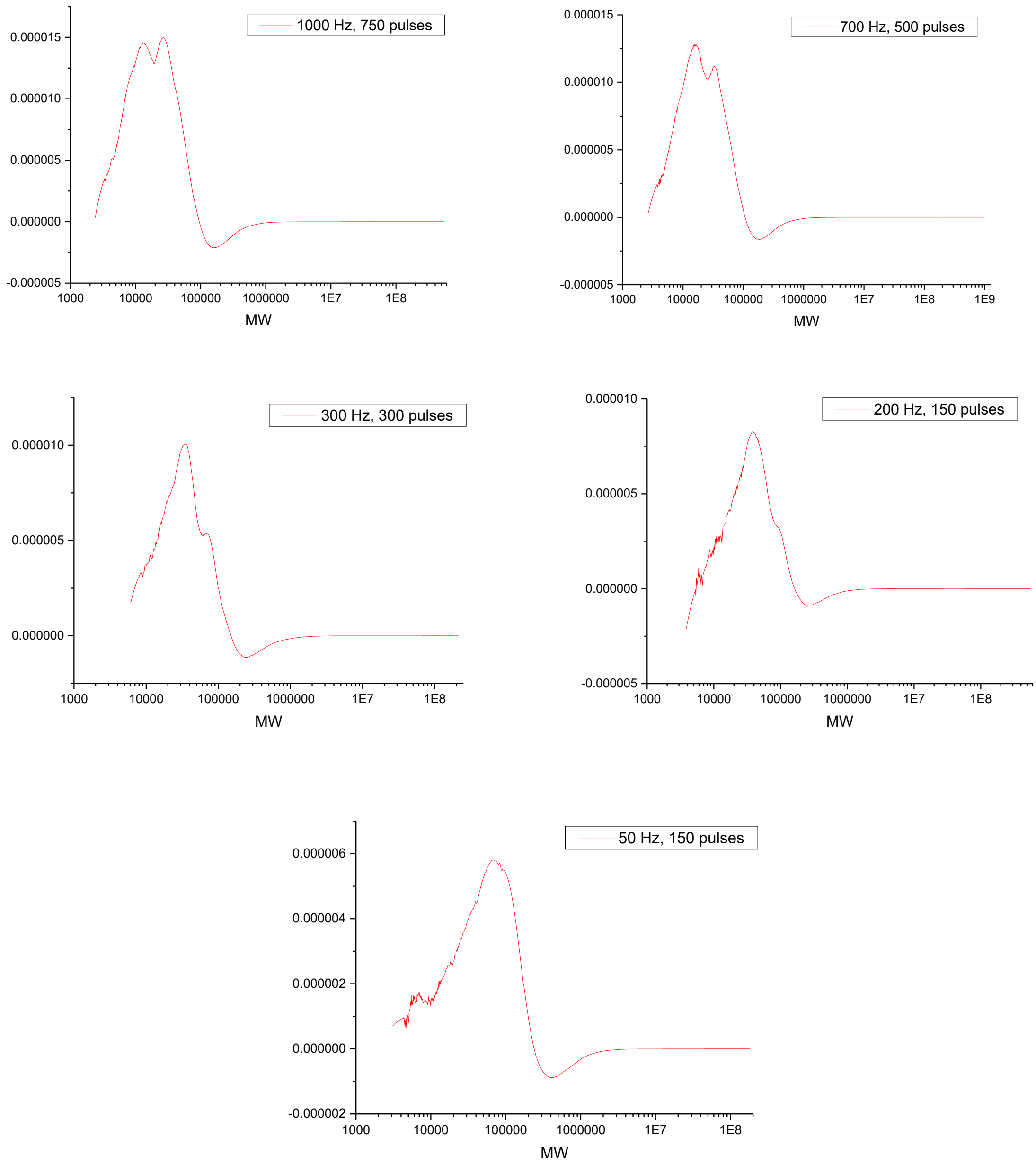

Figure S1 Representative first derivative PLP-SEC traces for experiments with decreasing pulse repetition rate. Graphs shown are obtained for PLP-SEC at 20 °C. Experiments at higher temperatures show an earlier breakdown of the typical overtone-type structures.

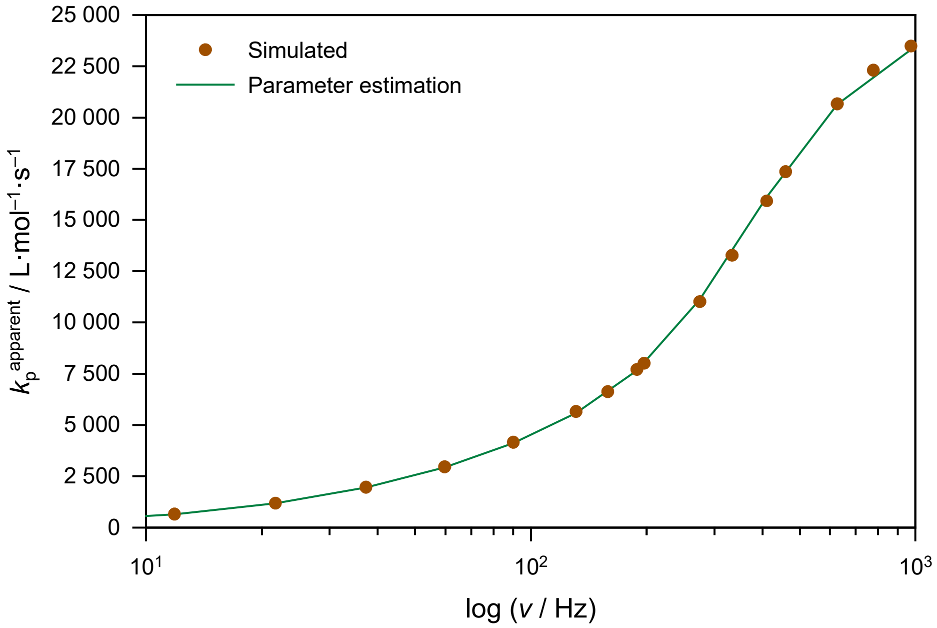

Figure S2 Example for parameter estimation testing. The plot shows simulated data (brown dots) for 50 °C which have in the following been fitted via Predici parameter estimation to test if the correct input parameters are obtained. As is seen, a good fit is obtained, returning the original input simulation data with very high accuracy (see Table S7 for more examples)

Table S7 Comparison of fit parameters obtained from Predici-parameter estimation with the original input parameters of the model. Ideally, if the parameter estimation procedure is robust, and the fit parameters are not correlated, then the fit procedure will returns the simulation input. If fit parameters were correlated than different set of values would be obtained. Error limits given are for 95% confidence intervals.

Simulation Input		***Parameter Estimation Return***	
$k_p^{average}$ / L·mol^{-1}·s^{-1}	k_p^{tert} / L·mol^{-1}·s^{-1}	$k_p^{average}$ / L·mol^{-1}·s^{-1}	k_p^{tert} / L·mol^{-1}·s^{-1}
333	10	333 ± 21	10.0 ± 7.8
1000	10	1070 ± 140	10.8 ± 1.9
3000	10	3880 ± 440	14.3 ± 2.7
5000	10	7210 ± 540	18.7 ± 2.9
333	50	334 ± 27	50.2 ± 7.1
1000	50	992 ± 27	49.8 ± 2.1
3000	50	3010 ± 350	50.6 ± 11.0
5000	50	5080 ± 180	52.4 ± 4.4