Supporting Information

Mechanochemical Degradation of Brush Polymers: Kinetics of Ultrasound-Induced Backbone and Arm Scission

Gregory I. Peterson,* Jinkyung Noh, Ki-Taek Bang, Hyunji Ma, Kyoung Taek Kim, Tae-Lim Choi*

Department of Chemistry, Seoul National University, Seoul 08826, Republic of Korea email: tlc@snu.ac.kr (TLC) and gpeterson@snu.ac.kr (GIP)

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1. Supporting Figures

polymer	DPw	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		k _{area} c (×10 ⁻² min ⁻¹)
	251	1.14 ± 0.14	1.28	1.28
PNB _n -EH	355	3.50 ± 0.51	2.95	2.95
	505	8.07 ± 1.24	7.94	7.61
	78	0.62 ± 0.02	0.63	0.60
PNB _n -g-PLA ₄₇	166	3.10 ± 0.05	3.19	3.03
	259	8.18 ± 0.14	8.47	8.45
PNB _n -g-PLA ₆₄	95	1.83 ± 0.03	1.86	1.88
	195	8.42 ± 0.37	9.13	9.13
	337	23.74 ± 1.11	23.30	24.89
PNB _n -g-PLA ₈₂	89	2.02 ± 0.01	2.71 ± 0.07	2.63
	221	10.72 ± 0.23	13.43 ± 0.45	12.80
	361	20.74 ± 0.42	30.50 ± 2.09	31.67
PNB _n -g-PS ₃₆	85	0.64 ± 0.03	0.60	0.57
	244	6.88 ± 0.14	8.16 ± 0.56	7.53
	313	10.65 ± 0.19	11.88 ± 0.27	11.53
PNB _n -g-PS ₅₀	101	1.24 ± 0.03	1.18	1.17
	258	8.63 ± 0.21	9.84 ± 0.72	10.04
	346	18.40 ± 0.26	22.58 ± 1.73	20.53
PNB _n -g-PS ₇₇	105	2.27 ± 0.03	2.29 ± 0.10	2.35
	239	11.66 ± 0.70	13.39	13.00
	300	19.31 ± 1.86	22.75	22.66

Table S1. Linear and brush polymer backbone degradation rate constant summary.

^aFirst order rate constant determined from a single retention time. Values are an average from three runs ± one standard deviation. ^bFirst order rate constant determined from a single retention time and resolved SEC traces. Values for k_{res} are reported for a single run unless that value fell outside of k_{RI} ±3 σ , then they are reported as averages ± one standard deviation. ^cFirst order rate constant determined from the peak area from resolved SEC traces. Values are reported for a single run.



Scheme 1. Synthesis of PLA (A) and PS (B) Macromonomers and their respective brush polymers (C).

polymer	M _w ^a (kDa)	$m{ heta}_{M}^{a}$	DP_{W^b}	arm length ^c (nm)	k_{area}^{d} (×10 ⁻⁵ min ⁻¹)
PNB ₇₈ -g-PLA ₄₇	262.0	1.04	78	16.8	1.30±0.45
PNB ₉₅ -g-PLA ₆₄	439.0	1.07	95	23.2	16.08±1.12
PNB ₈₉ -g-PLA ₈₂	528.1	1.07	89	29.7	30.88±1.94
PNB ₈₅ - <i>g</i> -PS ₃₆	315.3	1.04	85	9.0	2.08±1.03
PNB ₁₀₁ - <i>g</i> -PS ₅₀	516.4	1.05	101	12.6	2.90±0.92
PNB ₁₀₅ - <i>g</i> -PS ₇₇	844.2	1.06	105	19.5	15.89±2.16
PNB ₃₀₀ - <i>g</i> -PS ₇₇	2401	1.20	300	19.5	14.74±0.39

Table S2. Characterization of Molecular Weight and Arm Scission Rate Constants.

^aDetermined by SEC with MALS. ^bDetermined by dividing the M_w by the macromonomer M_w . ^cEqual to the macromonomer DP_w × repeat unit length of PLA (0.36 nm) or PS (0.253 nm). ^dFirst order rate constants determined from integration of peak area, see the Experimental section in the main text for more details. Values are an average of three runs ± one standard deviation.

2. Materials

The following were prepared and characterized as previously reported: polynorbornene (PNB)based polymers with 2-ethyl-1-hexyl side chains (PNB-EH),¹ 4-(2-hydroxyethyl)-4-azatricyclo [5.2.1.0(2,6)]dec-8-ene-3,5-dione (1),² 4-(Prop-2-yn-1-yl)-4-azatricyclo[5.2.1.0(2,6)]dec-8-ene-3,5-dione (2),³ and polystyrene (PS) with an azide end group (PS-N₃).⁴ Tetrahydrofuran (THF) that was used as polymerization solvent was distilled from sodium and benzophenone and was degassed via bubbling Ar through the solvent. Styrene was passed through a short plug of activated neutral alumina and degassed via bubbling Ar through the monomer before use. D,Llactide was recrystallized three times from toluene before use. All other reagents and solvents were used as obtained from commercial sources.

3. Characterization Methods

NMR: ¹H NMR spectra were recorded on a Varian/Oxford As-500 (500 MHz) spectrometer. *Size Exclusion Chromatography (SEC)*: The SEC setup utilized a Waters high pressure liquid chromatography (HPLC) pump (a 1515 pump was replaced with a 515 pump during the project), Waters 2707 autosampler with a loop volume of 100 μ L, and two Shodex gel permeation chromatography LF-804 size-exclusion columns maintained at 35 °C. For molecular weight characterization Wyatt DAWN-HELEOS 8+ multi-angle light scatter (MALS) and Wyatt OptiLab T-rEx refractive index (RI) detectors (both maintained at 35 °C) were used. The mobile phase

¹ Dutertre, F.; Bang, K.-T.; Loppinet, B.; Choi, I.; Choi, T.-L.; Fytas, G. Macromolecules 2016, 49, 2731-2740.

² Huang, Y.; Vezeridis, A. M.; Wang, J.; Wang, Z.; Thompson, M.; Mattrey, R. F.; Gianneschi, N. C. *J. Am. Chem. Soc.* **2017**, *139*, 15-18.

³ Bates, C. M.; Chang, A. B.; Momčilović, N.; Jones, S. C.; Grubbs, R. H. *Macromolecules* 2015, 48, 4967-4973.

⁴ Cho, A.; La, Y.; Shin, T. J.; Park, C.; Kim, K. T. *Macromolecules* **2016**, *49*, 4510-4519.

consisted of HPLC-grade THF with a 1 mL/min flow rate. Molecular weights were determined from light scattering using dn/dc values calculated from batch mode measurements of polymer solutions at different concentrations.

4. Synthesis

Reactions that deviated from reported protocols are summarized in **Scheme S1** and below.

4.1. Polylactide (PLA) Macromoners

PLA macromonomers were prepared using a slightly modified version of reported protocol.⁵ Specifically, **1** and D,L-lactide were added into a flame-dried 20 mL vial, sealed, and purged with Ar. After elevating the temperature to 130 °C, tin(II)-2-ethylhexanoate was added to the stirred solution. The solution was cooled down to RT after 2.5 –3 h with conversion around 95%, the product was dissolved in chloroform, filtered through celite to remove catalyst, precipitated into cold methanol, collected, and dried under reduced pressure. PLA macromonomers were generally obtained in 94 – 95% yield.

4.2. Polystyrene (PS) Macromonomers

PS macromonomers were prepared using a slightly modified version of reported protocol.³ Specifically, a Schlenk flask was charged with **2**, PS-N₃, and THF. A mixture of CuBr, N,N,N',N'', pentamethyldiethylene-triamine and THF was prepared and stirred in another flask for 15 min, then added into the Schlenk flask. The mixture was degassed with N₂ for 20 min and stirred for 24 h at 50 °C. After 24 h, chloroform was added into the mixture and then filtered through a column of basic alumina with dichloromethane to remove the remaining Cu. The residual mixture was precipitated into cold methanol, collected, and dried under reduced pressure. PS macromonomers were generally obtained in 89 – 90% yield.

4.3. Polymerization of Macromonomers

Ring-opening metathesis polymerization (ROMP) of PLA and PS macromonomers was carried out using a slightly modified version of reported protocol.⁶ Specifically, macromonomers was put into a 4 mL flame-dried vial, sealed with a septum, and purged with Ar. THF was added to the vial and three freeze-pump-thaw cycles were conducted to further degas the solution. A stock solution of Grubbs 3^{rd} -generation catalyst (G3) in THF was prepared in another Ar-purged 4 mL vial with septum. The desired amount of catalyst solution was rapidly added, via microsyringe, to the monomer solution (monomer concentration of 0.05 - 0.06 M) and stirred at room temperature for 0.5 - 16 h (with increasing time for increasing monomer-to-initiator ratio). Polymerizations were terminated with ethyl vinyl ether and polymers were obtained after precipitation into cold methanol, collection, and drying under reduced pressure. Monomer conversion always exceeded 90% and polymer yields ranged 73 – 94%.

⁵ Sveinbjörnsson, B. R.; Weitekamp, R. A.; Miyake, G. M.; Xia, Y.; Atwater, H. A.; Grubbs, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 14332-14336.

⁶ Lin, T.-P.; Chang, A. B.; Chen, H.-Y.; Liberman-Martin, A. L.; Bates, C. M.; Voegtle, M. J.; Bauer, C. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2017**, *139*, 3896-3903.

5. Ultrasonication Studies.

For sonication studies, we used a 20 kHz Sonics VCX-500 series sonication probe with an extender tip (1.25 cm tip diameter), calibrated according to literature procedures.⁷ Polymers (15 mg) were added to two-arm (fitted with rubber septa) Suslick flasks, sealed to the sonication probe, and purged with Ar for 15 min. In a separate sealed flask, Ar was bubbled through THF (inhibitor free HPLC-grade) for 15 min, then added to the Suslick flask (polymer concentration of 1 mg/mL). An Ar filled balloon was attached to the flask via a needle through the rubber septum. The Suslick flask was submerged in a cold bath maintained at -10 °C by a recirculating chiller (giving internal solution temperatures of ca. 10 °C during sonication). Polymer solutions were sonicated at 16.9 W/cm² using a pulse sequence of 1s "on", 4s "off" (all reported sonication times are based on total "on" time). Aliquots were withdrawn periodically and analyzed by SEC. Sonication experiments were conducted in triplicate.

6. More Details on Rate Constant Determination

In this section, we expand on the details provided in the Experimental section of the main text and show a representative example, specifically the data for PNB_{195} -*g*-PLA₆₄. The parent polymer concentration was estimated using the value of the RI signal at the ca. 13 min retention time corresponding to the peak maximum (P_{max}) retention time of the polymer at 0 min of sonication (indicated by the dashed line in **Figure S1**). The first-order rate constant (k_{RI}) was obtained by fitting the natural log of the RI signal versus sonication time. In general, all kinetics plots showed highly linear first order plots with high R² values.



Figure S1. (Left) RI SEC traces for PNB₁₉₅-*g*-PLA₆₄ with increasing sonication time and the P_{max} retention time indicated by the black dashed line. (Right) Linear first-order plot from which the rate constant (k_{RI}) for parent polymer backbone scission was acquired. Values are an average from three independent experiments with error bars representing ± one standard deviation.

This method is only valid if there is not significant overlap of the daughter fragments (lower molecular weight fragments generated during parent chain scission) at the 13 min retention time. Several methods were used to determine the extent of overlap. First, using the MALS detector, we calculated the molar mass at the 13 min retention time with increasing sonication time. At 0, 2, 4, 6, and 10 min of sonication, the molar mass at 13 min was 960, 955, 967, 969, and 976

⁷ Potisek, S. L.; Davis, D. A.; Sottos, N. R.; White, S. R.; Moore, J. S. J. Am. Chem. Soc. 2007, 129, 13808-13809.

kg/mol, respectively. Given that the molar mass does not significantly decrease, that supports that the half-molecular weight daughter fragments are not overlapping with this retention time. Second, we calculated first-order rate constants, k_{res} and k_{area} , using resolved SEC traces (**Figure S2**).



Figure S2. (Left) Resolved RI SEC traces for PNB₁₉₅-*g*-PLA₆₄ with increasing sonication time and the P_{max} retention time indicated by the black dashed line. (Middle) Linear first-order plot from which the rate constant (k_{res}) for parent polymer backbone scission was acquired. (Right) Linear first-order plot from which the rate constant (k_{area}) for parent polymer backbone scission was acquired.

The RI signal at 13 min was used to calculate k_{res} and the resolved peak area was used to calculate k_{area} . Comparison of k_{RI} with k_{res} and k_{area} (see **Table S1**) provides insight into the extent of the daughter fragments influencing the rate constant, as described in the main text.

7. Degradation with a mechanophore (from previous study)

We compared the rate constant for PNB₁₀₅-*g*-PS₇₇ arm scission (15.89 \pm 2.16×10⁻⁵ min⁻¹) to that of our previously reported PNB₂₇-*g*-mechanophore-PS₇₆ (shown in **Figure S3**; referred to as **P1** in our previous study).⁸ The arm scission rate for PNB₂₇-*g*-mechanophore-PS₇₆ was calculated from the average %AS of two independent sonication experiments and was equal to 20.0 ×10⁻⁵ min⁻¹. Thus, the arm scission rate with the mechanophore is about 1.3 time faster than without. This is comparable to the rate enhancement observed for linear and star polymers with the same mechanophore (compared to analogous linear and star polymers without mechanophores).⁹ Given the high selectivity for mechanophore) would be much smaller. Therefore, we expect that any differences in bonds breaking near the backbone-arm junction in PLA and PS arms would have a minor contribution to their observed difference in rate constant trends.

⁸ Peterson, G. I.; Lee, J.; Choi, T.-L. *TBD* **2019**, *TBD*, TBD.

⁹ Church, D. C.; Peterson, G. I.; Boydston, A. J. ACS Macro Lett. 2014, 3, 648-651.



Figure S3. Chemical structure for the PNB₂₇-*g*-mechanohpore-PS₇₆ and first order plot for arm scission.⁸

8. Limiting Length Values

We previously determined the M_{lim} for linear PS to be 13.8 kDa,⁸ this corresponds to a limiting length (L_{lim}) of 33.6 nm (repeat unit length of 0.253 nm). We determined the M_{lim} for linear PLA using our sonication conditions by sonicating a linear PLA sample with initial M_n of 20 kDa and followed the reduction in M_n over the course of 10 h of sonication (**Figure S4**). We fit the resulting data using **Equation 1**:¹⁰

$$M_t = M_{lim} + (M_{in} + M_{lim})e^{-kt}$$
(1)

where *t* is time, M_t is the molecular weight at a given time, M_{in} is the initial molecular weight, and *k* is a rate constant. The least square regression fit of our data gave a M_{lim} value of 7.75 kDa, which corresponds to L_{lim} a of 38.7 nm (repeat unit length of 0.36 nm).



Figure S4. Reduction in M_n for a linear PLA during sonication and fit used to estimate M_{lim} .

Plotting the rate constants against the arm length, corrected for the difference in L_{lim} values ($\Delta L_{lim} = L_{lim,x} - L_{lim,PS}$), leads to apparent convergence of the rate trends for PLA and PS arms (**Figure S5**).

¹⁰ Akyuz, A.; Catalgil-Giz, H.; Giz, A. T. *Macromol. Chem. Phys.* **2008**, 209, 801-809.



Figure S5. Arm scission rate constants plotted against arm length - ΔL_{lim} (i.e., $L_{\text{lim,x}}$ - $L_{\text{lim,PS}}$). PLA and PS arms have Red and Blue markers, respectively. Each data point represents the average value from three independent experiments. Error bars represent ± one standard deviation. Dashed line is for visual aid only.

9. SEC Traces

Note: Due to the use of two different GPC setups (due to pump failure) some retention times may not be directly comparable. This had no influence on our molecular weight characterization (we used MALS), nor kinetics analyses (the GPC setup was consistent for each time point of a given sonication experiment). The traces are provided primarily to show the shape of the distributions.



10. NMR

Representative ¹H NMR of a PLA macromonomer:



Representative ¹H NMR of a PS macromonomer:







Representative ¹H NMR of a PNB-g-PS brush polymer:







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