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# Comparison of Mechanochemical Chain Scission Rates for Linear versus Three-Arm Star Polymers in Strong Acoustic Fields

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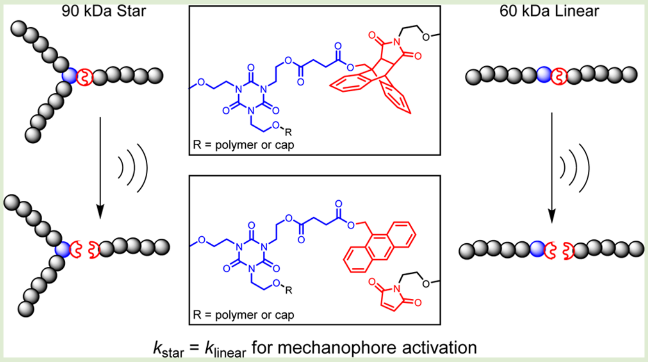
S *Supporting Information*

**ABSTRACT:** The effect of star versus linear polymer architecture on the rates of mechanochemically induced bond scission has been explored. We determined rate constants for chain scission of parent linear and star polymers, from which daughter fragments were cleanly resolved. These studies confirm a mechanistic interpretation of star polymer chain scission that is governed by the spanning rather than total molecular weight. We further demonstrate the preserved rate of site-selective mechanophore activation across two different polymer structures. Specifically, we observed consistent activation rate constants from three-arm star and linear polymer analogues, despite the $M_n$ of the star polymer being 1.5 times greater than that of the linear system.



Mechanochemistry involves transduction of mechanical input into chemical output by coupling force vectors with productive geometric distortions of functional groups.[1] Polymer mechanochemistry, specifically, uses macromolecular scaffolds to direct and distribute mechanical forces as a function of shape and composition of the polymer framework.[2,3] Perhaps the simplest chemical output that can arise from tensile forces within a polymer main chain is bond scission leading to fragmentation of the polymer. Understanding mechanochemical chain scission has important implications for multiple disciplines, considering that a number of physicochemical properties depend upon polymer molecular weight.

Studies focusing on the influence of polymer structure on mechanochemical reactivity have unveiled key correlations.[4−7] One of the most basic tenets for linear polymers in elongational flow fields is a linear relationship between chain scission rate and molecular weight.[8] Variations in polymer shape, however, give rise to changes in molecular weight distribution, which in turn can influence scission rates. For example, star polymers display an enhanced shear stability in comparison with linear polymer analogues of the same total molecular weight ($M_{total}$).[5,9] This effect is ascribed to the star polymers having a lower effective molecular weight that is roughly equivalent to two of the arms. This spanning region has a molecular weight ($M_{span}$) that is much lower than the $M_{total}$, thus the slower rate of chain scission.[5c]

One of the challenges to determining rate constants for specific chain scission events is that daughter fragments typically have molecular weights greater than the limiting molecular weight ($M_{lim}$) for chain scission. Therefore, commonly employed analyses of changes in ensemble averages for a polymer sample, such as molecular weight or viscosity, are not explicitly linked to chain scission in a single species (Figure 1). For example, Striegel and co-workers have studied ultrasound-induced chain scission in a series of star polymers and observed an apparent *increase* in observed rate constant upon prolonged sonication.[5c] This was explained by an increase in the number of polymer species present that were above $M_{lim}$ as the star polymers shed arms and an inability to distinguish between the reacting species when monitoring the average molecular weight of the mixture. Herein, we describe a quantitative assessment of rate constants for mechanochemical chain scission in complementary series of star and linear polymers and resolution of scission events between parent and daughter species.

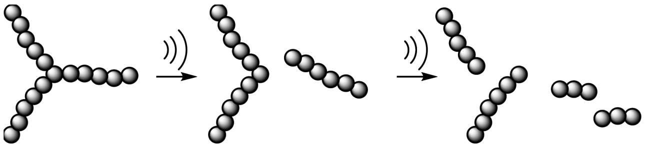


**Figure 1.** Generalized depiction of chain scission sequences in parent star and daughter polymer species.

To begin, we synthesized a series of well-defined linear and three-arm polymer counterparts as depicted in Figure 2. The linear analogues were designed to represent the "two-arm" daughter fragments resulting from hypothetical single-arm cleavage of the corresponding three-arm star polymer. Observed trends were found to be independent of either

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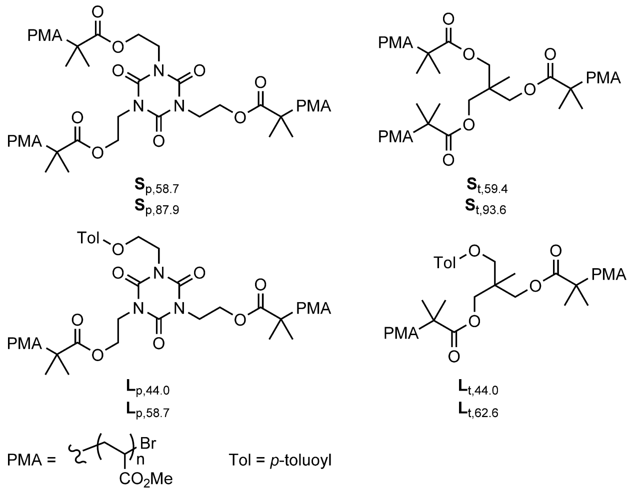

**Figure 2.** Structures of star and linear polymers used in this study. Subscripts indicate core geometry (planar or tetrahedral) and $M_n$ values. All PDIs were found to be <1.1 (see Supporting Information).

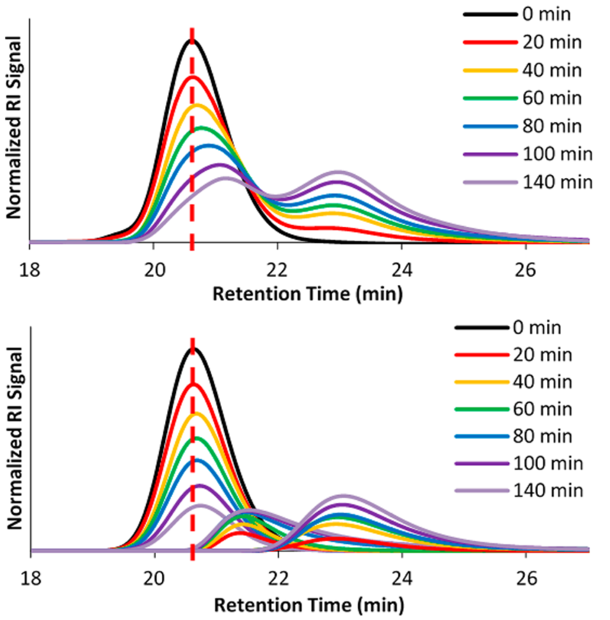

**Figure 3.** (top) GPC traces of $\mathbf{S}_{t,59.4}$ during ultrasonication. Sonication conditions: polymer concentration of 5 mg/mL in DMF, 13.8 W/cm$^2$, duty cycle of 1 s on 9 s off, $N_2$ atmosphere, 4 °C monitored internally. (bottom) Resolved GPC traces from nonlinear regression analysis of the chromatograms in the top plot. Dashed red lines indicate the retention time at which RI signal intensity was recorded for kinetic analyses.

**Table 1. Summary of $k_{RI}$ for Mechanochemical Chain Scission of Three-Arm Star and Linear Polymers.**

| polymer | $M_{total}$ (kDa) | $M_{arm}$ (kDa) | $k_{RI}$ ($\times 10^{-2}$ min$^{-1}$) |
|---|---|---|---|
| $\mathbf{S}_{p,58.7}$ | 58.7 | 19.6 | 1.02 ± 0.02 |
| $\mathbf{S}_{t,59.4}$ | 59.4 | 19.8 | 1.10 ± 0.02 |
| $\mathbf{L}_{p,44.0}$ | 44.0 | 22.0 | 1.26 ± 0.03 |
| $\mathbf{L}_{t,44.0}$ | 44.0 | 22.0 | 1.25 ± 0.08 |
| $\mathbf{S}_{p,87.9}$ | 87.9 | 29.3 | 2.44 ± 0.17 |
| $\mathbf{L}_{p,58.7}$ | 58.7 | 29.3 | 2.38 ± 0.12 |
| $\mathbf{S}_{t,93.6}$ | 93.6 | 31.2 | 2.66 ± 0.14 |
| $\mathbf{L}_{t,62.6}$ | 62.6 | 31.3 | 2.63 ± 0.06 |

[a] $M_{total}$ ($M_n$ values) determined by GPC analysis using multiangle laser light scattering (MALS) to give $M_w$ values from which $M_n$ values were calculated. $M_{arm}$ were assumed to be one-third $M_{total}$ for stars and one-half $M_{total}$ for linear polymers. Rate constants were calculated from linear regression of the Ln(RI signal intensity) at the $P_{max}$ retention time of the virgin sample versus ultrasonication "on time" and are an average of three runs ± one standard deviation.

planar or tetrahedral core geometries (vide infra). We used a "core-first" approach and atom-transfer radical polymerization to produce a series of polymers each with narrow polydispersity index (PDI).[10] Kinetic analyses were conducted using the method described by Florea.[11] This method involves following the refractive index (RI) signal intensity of a single section of the insipient portion of the gel-permeation chromatogram over the course of the sonication experiment. This approach more effectively distinguishes initial chain scission from scission of daughter fragments than the average molecular weight analysis developed by Malhotra and used by Striegel.[5c,12] A caveat of the Florea method, however, is that adequate resolution of polymer species by gel permeation chromatography (GPC) must be achieved.

Each linear and star polymer was subjected to sonication in DMF, and aliquots were analyzed by GPC over time. As a representative example, GPC traces of $\mathbf{S}_{t,59.4}$ are depicted in Figure 3 (top). The peak maximum ($P_{max}$) retention time before sonication was found to be 20.4 min (indicated by the dashed red line). Monitoring the RI signal intensity at that retention time over the course of the sonication experiment provided a first-order rate constant ($k_{RI}$) for the consumption of the polymer species with a molecular weight of $M_p$. The $P_{max}$ for each initial polymer remained consistent throughout the set of three runs, indicating to us that column drift was not significant.[13]

Applying the same sonication conditions and analyses to each of the polymers in the series provided $k_{RI}$ values as listed in Table 1. The trends are consistent with those observed by Striegel in which the $M_{arm}$, as opposed to $M_{total}$, of the polymer dictates the rate of chain scission.[5c] While two sequential chain scission events are operative in the mechanochemical degradation of three-arm star polymers, $k_{RI}$ for consumption of each star polymer closely matches that of the corresponding linear counterpart of equal $M_{arm}$. For polymers with $M_{arm}$ of ca. 20 kDa, $k_{RI}$ were all similar, ranging from 1.02 to 1.26 $\times 10^{-2}$ min$^{-1}$. Moreover, the differences in $k_{RI}$ correlated well with the slight differences in $M_{arm}$. The same general trend was observed from the polymers bearing ~30 kDa arms, with $k_{RI}$ clustered between 2.38 and 2.66 $\times 10^{-2}$ min$^{-1}$. Notably, an increase in *linear* polymer $M_{total}$ from $\mathbf{L}_{t,44.0}$ to $\mathbf{L}_{t,62.6}$ resulted in an approximately doubled value of $k_{RI}$. In contrast, increasing $M_{total}$ via a branch point to form a star polymer (cf. $\mathbf{L}_{t,44.0}$ versus $\mathbf{S}_{t,59.4}$) actually resulted in a slight reduction in $k_{RI}$, consistent with the reduction in $M_{arm}$.

A nonlinear regression analysis was used to resolve each GPC trace, which verified that the daughter fragments were not significantly contributing to the peak height at the retention time used for determining $k_{RI}$ (Figure 3, bottom). Using the resolved peaks, we calculated rate constants for scission of the initial polymer based upon the resolved initial $P_{max}$ retention time RI intensity ($k_{res}$) and total peak area ($k_{area}$) for that species. We found $k_{RI}$ to be in good agreement with $k_{res}$ and $k_{area}$ for each polymer.[13]

To investigate site-selective mechanophore activation as a function of polymer shape, we also prepared and analyzed a

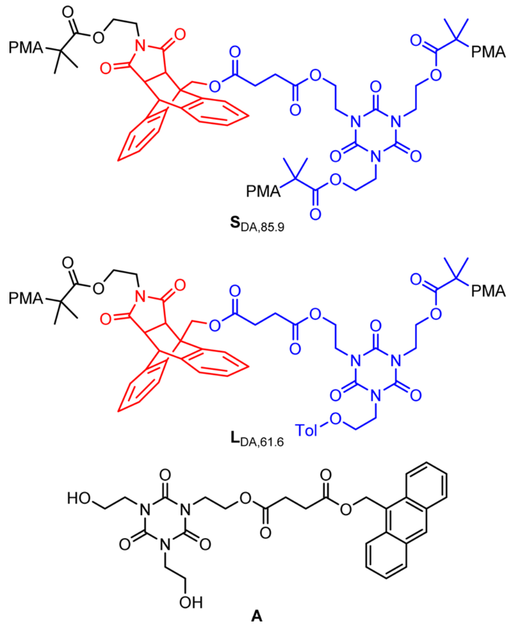

**Figure 4.** Mechanophore-containing star ($S_{DA,85.9}$) and linear ($L_{DA,61.6}$) polymers and PL control compound **A**. Mechanophore is highlighted in red, and core is highlighted in blue.

linear ($\mathbf{L}_{DA,61.6}$) and star polymer ($\mathbf{S}_{DA,85.9}$) pair that each contained an anthracene-maleimide Diels–Alder adduct mechanophore (Figure 4). Importantly, the average $M_{arm}$ was similar in each polymer. The mechanophore, which has been extensively studied by Bielawski and co-workers, is capable of mechanochemical UV–vis and photoluminescence (PL) "turn-on" response upon mechanically facilitated cycloreversion to generate an anthracene moiety.[14]

After subjecting $\mathbf{L}_{DA,61.6}$ and $\mathbf{S}_{DA,85.9}$ each to sonication as described above, the formation of anthracene was confirmed by UV–vis (Figure 5A) and PL spectroscopies (Figure 5B). Although the UV–vis spectra were consistent with formation of anthracene, control experiments revealed increases in solution optical density upon sonication of PMA (absent mechanophore). Although background corrections could be made, the optical density was dependent upon the extent of chain scission, which occurred at different rates and via different mechanisms for unfunctionalized PMA versus mechanophore-containing polymers (vide infra). PL experiments, however, confirmed consistent emission intensity over 60 min of sonication time (Figure 5C) for an anthracene-containing control (**A**) sonicated in the presence of $\mathbf{L}_{P,58.7}$. This confirmed the stability of anthracene to sonication and circumvents issues with increased optical density upon sonication of polymer solutions. Additionally, we observed a linear correlation between PL intensity and concentration of **A** over the concentration range relevant to our kinetic studies (Figure 5D).

Monitoring the consumption of initial polymer via GPC-RI, and production of anthracene via PL spectroscopy (to give $k_{PL}$), provided corroborating data for consistent chain scission rate constants between the two polymer structures. As in the previous series, we found $k_{RI}$ for the linear and star analogues to be very similar, consistent with their similar $M_{arm}$ values (Table 2). Additionally, the $k_{PL}$ values for each polymer were also similar to one another and to the $k_{RI}$ values. The similarity between the $k_{RI}$ and $k_{PL}$ values is consistent with high selectivity for initial chain scission occurring at the mechanophore.

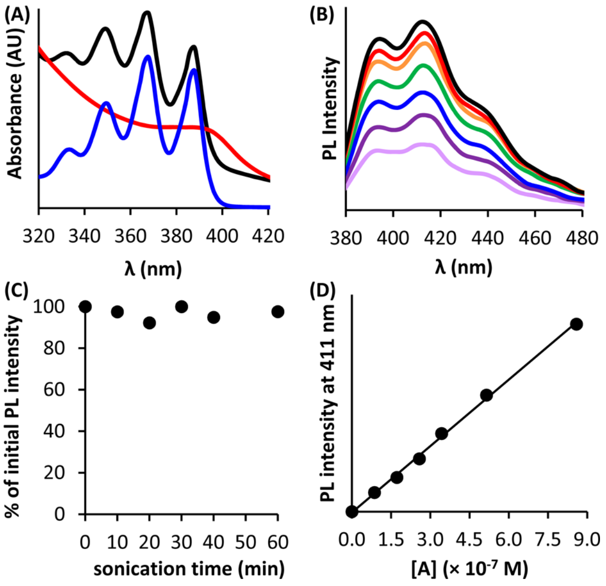

**Figure 5.** (A) UV–vis spectra in DMF of $S_{DA,85.9}$ before (red) and after (black) sonication and a small molecule control (blue);[13] (B) PL spectra in DMF of $L_{DA,61.6}$ upon increasing sonication time (10–40 min, 5 min increments bottom-to-top); (C) % of initial PL intensity with increasing sonication time of a mixture of $L_{p,58.7}$ and **A** in DMF; (D) PL intensity versus concentration of **A** in the presence of $L_{p,58.7}$ ($R^2$ = 0.9981).

### Table 2. Rate Constants for Mechanochemical Chain Scission for $S_{DA,85.9}$ and $L_{DA,61.6}$[a]

| polymer | $M_{total}$ (kDa) | $M_{arm}$ (kDa) | $k_{RI}$ (× $10^{-2}$ min$^{-1}$) | $k_{PL}$ (× $10^{-2}$ min$^{-1}$) |
|---|---|---|---|---|
| $\mathbf{S}_{DA,85.9}$ | 85.9 | 28.6 | 3.13 ± 0.11 | 3.20 ± 0.14 |
| $\mathbf{L}_{DA,61.6}$ | 61.6 | 30.8 | 3.27 ± 0.38 | 3.26 ± 0.09 |

[a] $M_{total}$, $M_{arm}$, and $k_{RI}$ were determined as described above. Rate constants via PL ($k_{PL}$) were calculated from linear regression of the Ln(PL intensity at 411 nm) versus ultrasonication "on time". Rate constants are an average of three runs ± one standard deviation.

The inclusion of the mechanophore resulted in a discernible increase in $k_{RI}$, (cf. Tables 1 and 2). Specifically, polymers with $M_{arm}$ values near 30 kDa clearly had $k_{RI}$ values less than those observed from the mechanophore-containing polymers. To our knowledge, direct comparisons of rate constants for this mechanophore versus PMA homopolymers have not been reported. However, the relative increase in rate constant upon inclusion of the mechanophore in these studies is consistent with those reported by Moore and co-workers for investigation of cyclobutane-based mechanophores.[8b]

In summary, we report precise investigations of mechanochemical chain scission rates in linear and three-arm star polymers. Our results are consistent with previous chain scission models in which the scission rate is governed by the length of any two arms emanating from the core. By resolving daughter fragments from the analysis and incorporating a fluorogenic "turn-on" mechanophore, we have provided kinetic analysis for specific scission events. These results provide quantitative guidelines for augmenting the mechanochemical reaction rates of macromolecules through control of the overall polymer architecture. Importantly, we observed nearly identical rate constants for activation of a mechanophore incorporated into structurally varied polymers of significantly different molecular weights.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Detailed experimental procedures, characterization of all new compounds, kinetic data for sonication experiments, and additional rate constant determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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