

The Role of Mass and Length in the Sonochemistry of Polymers

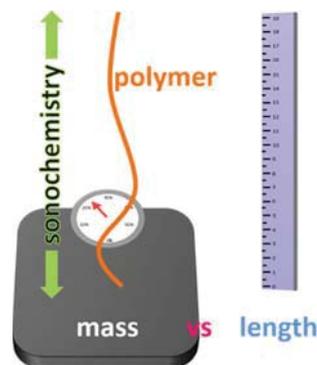
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ABSTRACT: The ultrasound-induced cleavage of macromolecules has become a routine experiment in the emerging field of polymer mechanochemistry. To date, it has not been conclusively proven whether the molecular weight of a polymer or its contour length is the determining factor for chain scission upon ultrasonication. Here we report comparative experiments that confirm unequivocally that the contour length is the decisive parameter. We utilized postpolymerization modifications of specifically designed precursor polymers to create polymers with identical chain length but different molecular mass. To demonstrate the universality of the findings, two different polymer backbones were utilized—poly(styrene) and poly(norbornene imide alkyne)—whose molecular weights were altered by bromination and removal of pendant triisopropylsilyl protecting groups, respectively. Solutions of the respective polymer pairs were subjected to pulsed ultrasound at 20 kHz and 10.4 W/cm² in order to investigate the chain scission trends. The effects of cleavage and sonochemical treatments were monitored by size exclusion chromatography. In both series, experimental data and calculations show that the molecular weight reduction upon sonication is the same for polymers with the same contour length.



Inspired by biological transduction mechanisms, such as mechanosensory pathways, the field of mechanochemistry has developed into a burgeoning area of science that aims to bestow upon materials the ability to transform a mechanical stimulus into a usable chemical potential.^{1–5} In recent years, polymeric materials have become a substrate of choice for mechanochemistry, both in solution and in the solid state.³ Polymers are particularly attractive thanks to their rich functionality and the ability to tailor their properties by tuning the chemistry and architecture of the macromolecules. One strategy to harness mechanical force and purposefully transduce it into a desirable response relies on incorporating weak bonds within the polymer. These stress-reactive moieties, coined mechanophores, cleave upon mechanical activation to form reactive species that can, for instance, further catalyze a reaction,⁶ change the pH,⁷ or induce a color change.^{8–10}

Beyond obvious macroscopic mechanical activation methods (e.g., mechanical testing in tension or compression), one widespread strategy consists in applying ultrasound to polymer solutions in order to elicit macromolecular chain scission.^{11,12} This methodology, referred to as sonochemistry, is particularly convenient to evaluate novel mechanophores, as it requires only small quantities of material and permits one to rapidly establish the responsiveness of new mechanoresponsive motifs upon integration into a macromolecule of choice. Indeed, the use of ultrasound to induce polymer chain cleavage predates the first studies on rational mechanophore design,^{12–14} and

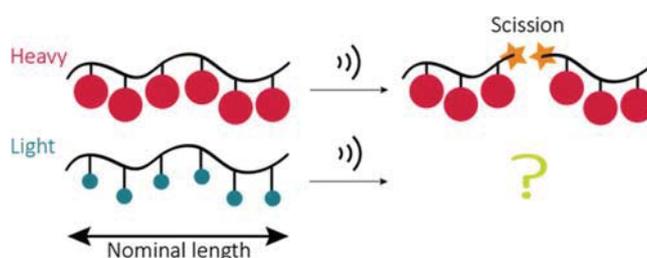
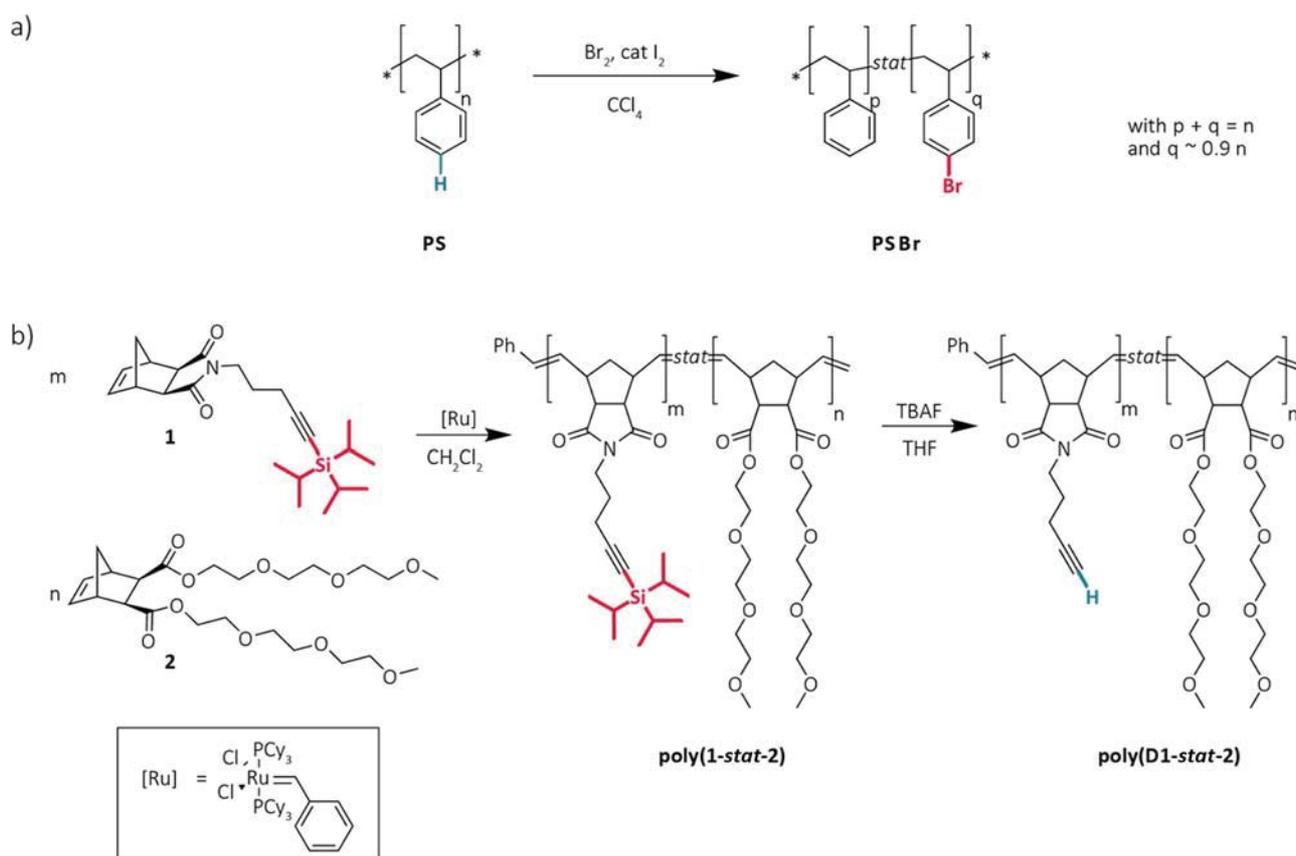


Figure 1. Schematic representation of polymer pairs with identical chain length but differing mass. To date, it has not been conclusively proven whether the molecular weight of a polymer or its contour length determines the possibility of chain scission upon ultrasonication.

such sound waves are well known to cause polymer degradation through extensional flow.¹⁵ Ultrasonic pressure waves are responsible for the growth of cavitation bubbles, whose violent collapse induces a vast amount of shear forces upon the polymer chains,^{16–18} causing rapid uncoiling and ultimately scission.^{3,12,19,20} Seminal contributions, by Schmid and Rommel and later by others,^{20,21} demonstrated that the molecular weight distribution of a polymer solution evolves toward lower masses upon sonication until a plateau is reached, meaning that no

Scheme 1. (a) Electrophilic Bromination of Poly(styrene) (PS) To Afford PSBr; (b) Copolymerization of Monomers 1 and 2 To Afford poly(1-*stat*-2) and Its Deprotection Using Tetrabutylammonium Fluoride (TBAF) To Give poly(D1-*stat*-2)



further chain scission of the polymer chains occurs. At this point, the number-average molecular weight reaches a value known as the limiting molecular weight (M_{lim}). M_{lim} depends to some extent upon the experimental conditions (solvent, dissolved gas, temperature, ultrasound frequency and intensity, etc.).^{3,22–24} Also, it is important to differentiate the notions of cutoff molecular weight and that of M_{lim} . While the two values are related, they are not identical. The cutoff molecular weight is a strict value given by the experimental conditions below which cavitation-induced extensional flow will not lead to chain scission. In contrast, M_{lim} is the measured experimental value at the end of the ultrasonication and will also depend on the initial molecular weight distribution.²⁵ The present study tries to assess whether a cutoff molecular weight is a sensible value or whether it should rather be replaced by a cutoff degree of polymerization.

Because of the technological relevance of processes that involve ultrasound, many polymers that have been used in sonochemical experiments have been commodity products.^{12–15} Even for polymers comprising specifically designed mechanophores, most research groups have focused on known polymer backbones so as not to complicate the results. However, in such systems, it is impossible to dissociate the effects of contour length and mass in chain scission, as the overall molecular mass and the contour length are directly correlated with the number of repeat units. Kulicke and co-workers reported an attempt to deconvolute mass and length in cellulosic materials.²⁶ However, these systems were relatively ill-defined and did not allow for an accurate molecular weight to be measured. In a series of recent compelling studies, Peterson, Boydston, and co-workers experimentally analyzed and modeled the mechanochemical

degradation of mechanophore-free and mechanophore-bearing star polymers extending the understanding to more complex architectures.^{27,28} In their work, the overall mass of the polymer was increased while the end-to-end distance remained virtually identical. In such star polymers, the mass increase is decoupled from the arms, meaning that the mass distribution is not homogeneous along the chain but rather locally increased at the center of mass by the third arm. These results are highly valuable and point toward a length-dominated scission. However, they do not permit a definitive conclusion as to whether mass or length is the determining factor.

In the present contribution, we report comparative ultrasonication experiments using polymers with identical contour length but different molecular mass. This was achieved by postpolymerization modifications of specifically designed poly(styrene) (PS) and poly(norbornene imide alkyne), whose molecular weights were altered by bromination and removal of pendant triisopropylsilyl protecting groups, respectively (Scheme 1). The introduction or removal of heavy side chains allows one to conserve a given chain length, while increasing or reducing the overall mass of the polymer significantly. Consequently, this strategy is a powerful way to decouple some of the key parameters in sonochemistry and ultimately to help get a better understanding of mechanical stress transfer down to the molecular level.

The first polymer pair investigated relied on the aromatic bromination of poly(styrene), with the notion that the bromine atoms considerably increase the weight of macromolecular chains. Electrophilic bromination at the *para*-position of the aromatic groups in each monomer unit results in a 75% weight gain (from 104 to 183 g/mol), but smaller changes of the number-average

molecular weight (M_n) of PS can be achieved by incomplete bromination. PS is highly attractive and convenient as a model system because (i) its sonochemistry has been thoroughly investigated and (ii) narrow molar mass dispersity (\mathcal{D}) standards of various M_n are commercially available. Here, two PS standards were utilized: a polymer with a “short” chain length, PS-S ($M_n = 13\,000$ g/mol) and one with a “long” one, PS-L ($M_n = 42\,000$ g/mol). These values were chosen to be significantly below and above some of the reported values for $M_{lim,PS}$ ca. 25 000–30 000 g/mol under similar conditions.^{22,23,29}

Both polymers were brominated in the *para*-position in the presence of catalytic amounts of iodine to afford the “heavy” version of the polymer, PSBr (Scheme 1a, See Supporting Information for details). Table 1 summarizes the compositions,

Table 1. Number-Average Molecular Weight and Dispersity Values of Poly(styrene) Polymers

sample	M_n^a (g/mol)	\mathcal{D}^a	bromination efficiency ^b (%)
PS-L	42 000	1.05	
PSBr-L	70 000	1.09	90
PS-S	13 000	1.04	
PSBr-S	22 000	1.04	92

^aDetermined by size exclusion chromatography (SEC) using light scattering detection. ^bDetermined by ¹H NMR spectroscopy.

M_n , and \mathcal{D} of the polymers before and after electrophilic bromination. A weight gain of 67% and 69% respectively was observed upon bromination of PS-L and PS-S and afforded PSBr-L ($M_n = 70\,000$ g/mol) and PSBr-S ($M_n = 22\,000$ g/mol), respectively. These values account for a bromination efficiency of ca. 90%, as was determined by ¹H NMR spectroscopy (Figures S1 and S2). Furthermore, a model bromination reaction was carried out under identical conditions on PS with an M_n of 2000 g/mol. The low molecular weight permitted MALDI-TOF spectrometry (Figure S3), which corroborated this bromination efficiency. It is important to reiterate that within the two pairs—PS-L/PSBr-L and PS-S/PSBr-S—the chain length remains unchanged upon bromination.

A second system was synthesized based on poly(norbornene)s bearing heavy pendant groups that can be cleaved at will. To ensure a significant mass loss, a norbornene imide with pendant triisopropylsilyl-protected (TIPS-protected) alkyne **1** was synthesized (see Supporting Information for details). This monomer was chosen because of the sizable 41% weight loss that occurs upon cleavage of the bulky TIPS protecting group with tetrabutylammonium fluoride (from 385 to 229 g/mol). Monomer **1** was therefore homopolymerized in the presence of benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs’ first-generation catalyst) to afford poly(**1**) with a high molecular weight of 130 000 g/mol (Scheme 1b, $n = 0$, Table 2).³⁰ Unfortunately, upon deprotection, the resulting polymer poly(D1) proved insoluble in tetrahydrofuran and acetonitrile and could therefore not be used for sonochemical experiments in these common solvents. To improve the solubility, **1** was copolymerized with a norbornene bearing two triethylene glycol (TEG) ester chains (**2**) with different amounts of catalysts to afford copolymers poly(**1-stat-2**), in which the residues of **2** account for approximately 20 mol % of the monomer residues. Here again, two chain lengths were chosen for the poly-(norbornene): a short one poly(**1-stat-2**)-S ($M_n = 21\,000$ g/mol) and a long one poly(**1-stat-2**)-L ($M_n = 80\,000$ g/mol). The target M_n for poly(**1-stat-2**)-L was chosen by conjecturing that

Table 2. Number-Average Molecular Weight, Dispersity Values, and Composition of Poly(norbornene) Polymers

sample	M_n^a (g/mol)	\mathcal{D}^a	mol % of 1 ^b	mol % of 2 ^b
poly(1)	130 000	1.4	100	
poly(1-stat-2)-L	80 000	1.8	78	22
poly(D1-stat-2)-L	40 000	1.9	78	22
poly(1-stat-2)-S	21 000	1.2	71	29
poly(D1-stat-2)-S	16 000	1.3	71	29

^aDetermined by SEC relative to poly(styrene) standards. ^bCalculated from ratios of characteristic signals in the ¹H NMR spectra.

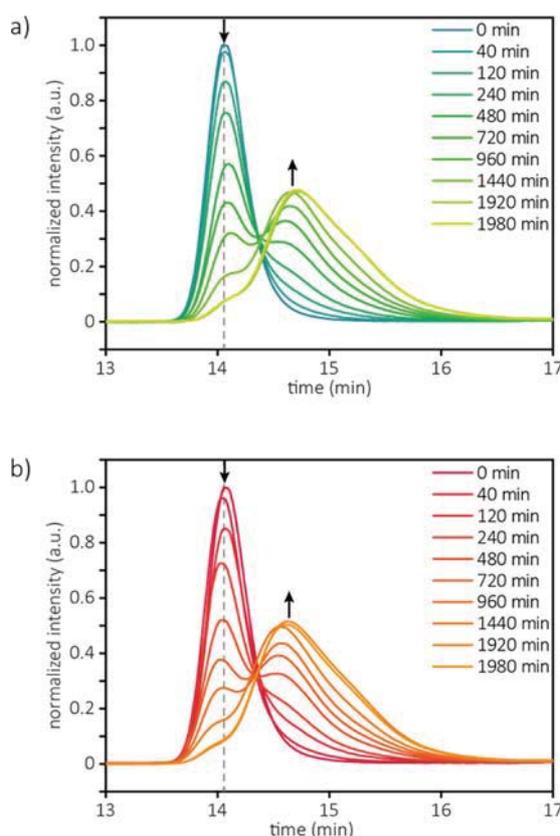


Figure 2. Size exclusion chromatograms (SECs) showing the bimodal mass distribution appearance for (a) PS-L and (b) PSBr-L upon sonication of solutions of these polymers in THF for the times indicated in the graphs. Dashed gray lines indicate P_{max} (the peak maximum retention time before sonication) at which the RI signal was recorded for kinetic analysis.

a polymer with a M_n significantly in excess of twice the $M_{lim,PS}$ should undergo scission and subsequently, verifying this assumption by observing the decrease in M_n upon sonication down to a $M_{lim,poly(1-stat-2)}$ (*vide infra*). The latter experimental value was then determined to choose the target M_n for poly(**1-stat-2**)-S. Table 2 summarizes the compositions, M_n , and \mathcal{D} of the polymers before and after deprotection. An apparent weight loss of 50% and 23% respectively was observed by SEC upon deprotection of poly(**1-stat-2**)-L and poly(**1-stat-2**)-S, resulting poly(D1-stat-2)-L and poly(D1-stat-2)-S, respectively (where L and S represent series with longer and shorter contour length, respectively). These values differ a bit from the theoretically expected weight loss (ca. 30%) but can be explained with conformational differences of the protected and deprotected polymers in solution, which in turn impact the SEC experiments (folding, polarity, etc.). Gratifyingly, \mathcal{D} was virtually not altered

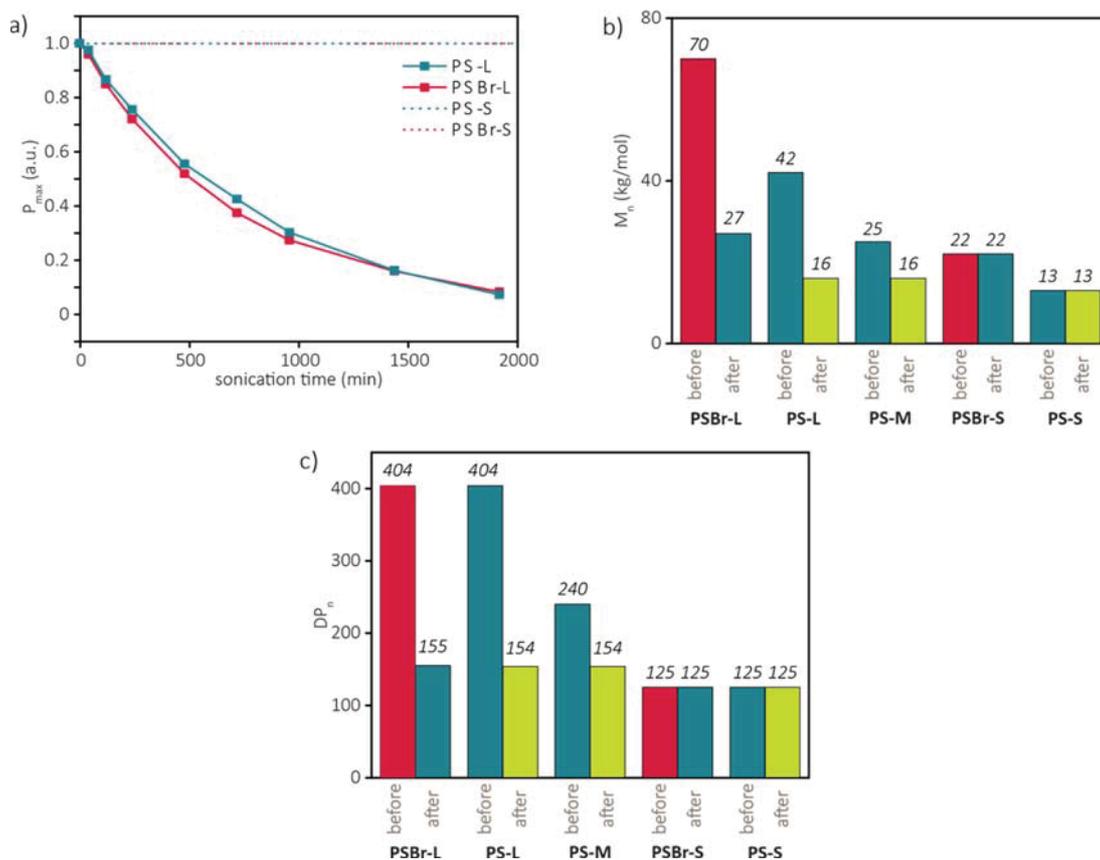


Figure 3. (a) Evolution of the RI intensities at P_{\max} retention time for each SEC trace as a function of sonication time of solutions of PSBr-L (red squares), PS-L (cyan squares), PSBr-S (red dashed line), and PS-S (cyan dashed line). The solid lines represent the exponential decay fits for PSBr-L (red) and PS-L (cyan). Degradation rates were fitted to 1.4×10^{-3} and $1.2 \times 10^{-3} \text{ min}^{-1}$, respectively. Variation of (b) the number-average molecular weight and (c) the number-average degree of polymerization before and after sonication for 1920 min at 10.4 W cm^{-2} PSBr-L, PS-L, PS-M, PSBr-S, and PS-S.

upon deprotection, which allows for a direct comparison between the TIPS-protected and the deprotected polymers.

Upon exposing solutions of the polymers (0.75 mg/mL in THF) to ultrasound (for 1980 min of effective sonication time at a power density of 10.4 W cm^{-2}), the M_n of PS-L and PSBr-L both decreased with time. A similar behavior was observed for PS-M ($M_n = 25\,000 \text{ g/mol}$). This PS standard was taken as an intermediate length system and additional data point. Size exclusion chromatograms show the gradual appearance of a lower-molecular-weight fraction and a (transient) bimodal mass distribution (Figure 2 and Figure S10). This behavior is consistent with preferential chain scission near the midpoint of the polymer and is in agreement with the reported ultrasound-induced degradation of PS of molecular weights with narrow \bar{D} .³¹ Plots of the number of scission events (RI intensity at the peak maximum retention time before sonication, P_{\max}) as a function of sonication time show the same trend (Figure 3a), and kinetic analyses (Figure S10), conducted by fitting an exponential function to these values,^{32,28} revealed first-order kinetics with virtually identical rate constants (1.4×10^{-3} and $1.2 \times 10^{-3} \text{ min}^{-1}$, respectively). The data show unequivocally that PS-L and PSBr-L, which have the same nominal length but differ in effective mass, exhibit identical scission characteristics upon ultrasonication in solution. This observation is further confirmed by a comparison of the decrease in M_n (Figure 3b) and even more so by the observation that the DP_n values are identical for both systems at the initial and final time points

(Figure 3c). When the corresponding solutions of the shorter polymer chains PS-S and PSBr-S were exposed to ultrasound, the SEC remained unchanged (Figure 3 and Figure S11), indicating that as expected based on M_{lim} 's previously established for PS-L and PSBr-L, no cleavage occurred. For the sake of comparison, the data for PS-M was also included in Figure 3b,c. It is important to notice the crossover between M_n . While PS-L and PS-M go down to ca. 16 000 g/mol, PSBr-S, whose mass is higher but DP_n is lower, remains unaffected. This result clearly depicts a situation where the contour length of the polymer chain is the main parameter of a stretch-and-break mechanism whereby the frictional forces exerted by the solvent upon the chains and velocity gradients obtained during cavitation are responsible for chain scission.³³

Similar experiments were conducted with poly(1-stat-2)-L, poly(D1-stat-2)-L, poly(1-stat-2)-S, and poly(D1-stat-2)-S. In the case of poly(1-stat-2)-L and poly(D1-stat-2)-L, unlike PS-L and PSBr-L, the size exclusion chromatograms do not display the formation of a secondary peak. Instead, gradual shifts toward longer elution times can be discerned (Figure 4) as a result of the broader molecular weight distributions.³⁴ However, the SEC traces clearly reveal a parallel decrease of the M_n upon sonication of poly(1-stat-2)-L and poly(D1-stat-2)-L (Figure 5a) and an apparent narrowing of \bar{D} over time (Figure 5b). In the case of poly(1-stat-2)-L, \bar{D} decreased from 1.8 to 1.3, whereas a decrease of \bar{D} from 1.9 to 1.6 was observed for poly(D1-stat-2)-L. The observed reduction of \bar{D} over time

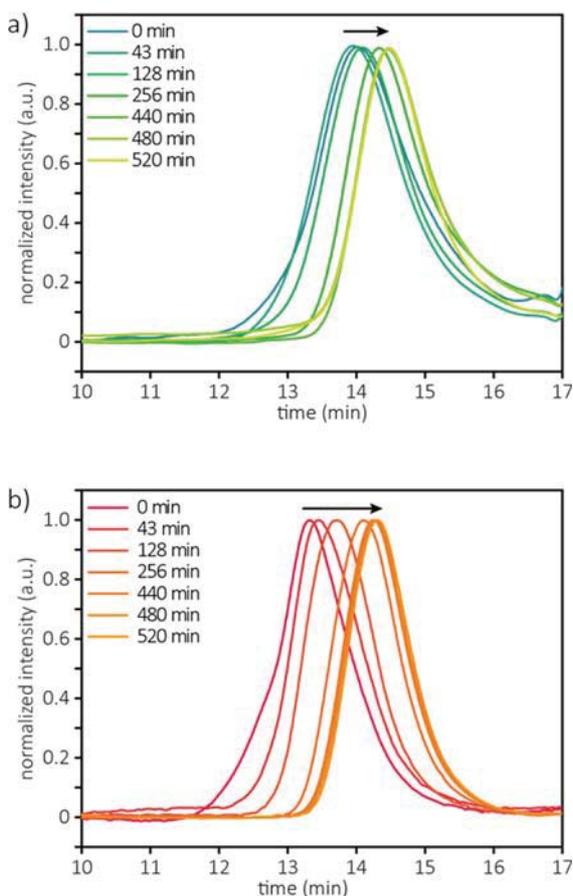


Figure 4. Size exclusion chromatograms showing the decrease of molecular weight for (a) poly(D1-stat-2)-L and (b) poly(1-stat-2)-L upon sonication. The data were normalized to the peak maximum of the chromatogram at 0 min.

appears to indicate that the longer chain molecules are cleaved more rapidly than the shorter ones.¹¹ In this case, kinetic analyses were conducted by following the time evolution of the chain length distribution. Also in this case, identical rate constants ($k \approx 8 \times 10^{-4} \text{ min}^{-1}$) for ultrasound-induced chain scission were determined by plotting $dM_n/dt = k(M_n - M_{lim})$ and fitting the data to a single-exponential decay function (Figure 5c). Thus, also in the case of the poly(norbornene) system, the data unequivocally show that the determining factor in the sonochemically induced chain cleavage of polymers is the contour length.

The combined results for poly(styrene) and poly(norbornene) can mechanistically be explained using the model developed by Okkuama and Hirose.³⁵ According to their approach, linear polymer chains break when the shear forces created by collapsing cavitation bubbles overcome the bond strength. The collapse of a bubble causes a linear chain to stretch, and the maximum tension occurs at the middle of the chain. Chains with identical chemical bonds along the backbone and identical length will thus undergo the same scission rate. Chains that are too short cannot be subjected to a sufficient shear rate and thus do not undergo a scission. The results were further simulated by means of a kinetic model, i.e., by applying mass balance equations for polymer chains of all lengths and relying on few very simple assumptions. The model uses an approach similar to that proposed by Glynn et al.²⁵ for linear polymers and extended to star polymers by Peterson and Boydston,²⁷ which has been abundantly used in the

literature.³⁶ Our modeling strategy, however, differs slightly because it permits to obtain the time evolution of the polymer chain length distribution and not simply its evolution in terms of the number of scission events. The detailed equations are reported in the Supporting Information. Chain scission events are modeled as first-order kinetic reactions. The reaction rate constant is assumed to be a linear function of the difference between the chain length (number of monomer units) and a cutoff length, below which no scission occurs. The length distribution of chain fragments generated by a scission of a given chain is assumed to be Gaussian, centered at the center of the chain. The variance of the distribution was set to about 20% of the chain length.

The kinetic model developed was first applied to the experimental data of the PS system with a narrow molecular weight distribution (Figure S14a). The cutoff molecular weight was set to 20 000 g/mol. While a common reported value for cutoff is typically 30 000 g/mol, one should consider that the sonication parameters heavily influences cavitation and subsequently efficiency.²² The simulation results allowed to determine the variance of the Gaussian fragment distribution. It is clear that the model can capture well the time evolution of the molecular weight distribution of PS after two cycles of sonication. A second PS sample with a much broader molecular weight distribution (Figure S14b) was simulated, and the model was also capable of quantitatively accounting for the effect of sonication on the degradation of the molecular weight distribution. Not surprisingly, the model is also able to capture precisely the degradation behavior on PS-L, as shown in Figure 6a. The differences observed are in the low molecular weight part of the chromatograms, where the model underpredicts the concentration of short chains. This might be a consequence of the model neglecting peak broadening in the SEC columns. The behavior of the PSBr-L is essentially identical.

The simulation results of the experimental data of poly(1-stat-2)-L and poly(D1-stat-2)-L are shown in Figure 6b,c and Figure S15, respectively. The simulations were carried out for both polymers under the assumption that the critical cutoff length is given by a DP of ca. 110 for poly(1-stat-2)-L, which corresponds to a molecular weight of ca. 40 000 g/mol and a DP of ca. 90 in the case of poly(D1-stat-2)-L, corresponding to a molecular weight of ca. 20 000 g/mol. The discrepancy between the two cutoff values could be a consequence of the larger than expected mass loss of the polymer upon deprotection and the generally poorer solubility of poly(D1-stat-2)-L. The model can capture well the time evolution of the number-average molecular weight and of the entire molecular weight distribution for the protected polymer. In the case of the deprotected polymer, the model offers a good prediction of the time evolution of the number-average molecular weight but generally underestimates the dispersity of the distributions, especially for the later stages of sonication.

While numerous literature reports had alluded to the importance of polymer length in sonochemistry, no definitive proof had been put forth regarding the effect of mass and length in the sonochemical elongational flow. Moreover, the great majority of papers in the field to date have referred to a cutoff molecular weight M_{lim} below which no chain scission was shown to occur. Our systematic study of specifically designed series of polymers has confirmed that there exists in fact a cutoff degree of polymerization, below which the polymer chains do not break. This finding was demonstrated by decoupling the effects of length and molecular weight through a change in the molar mass of the repeating unit and proving that the degradation rates remain identical for both PS and poly(norbornene).

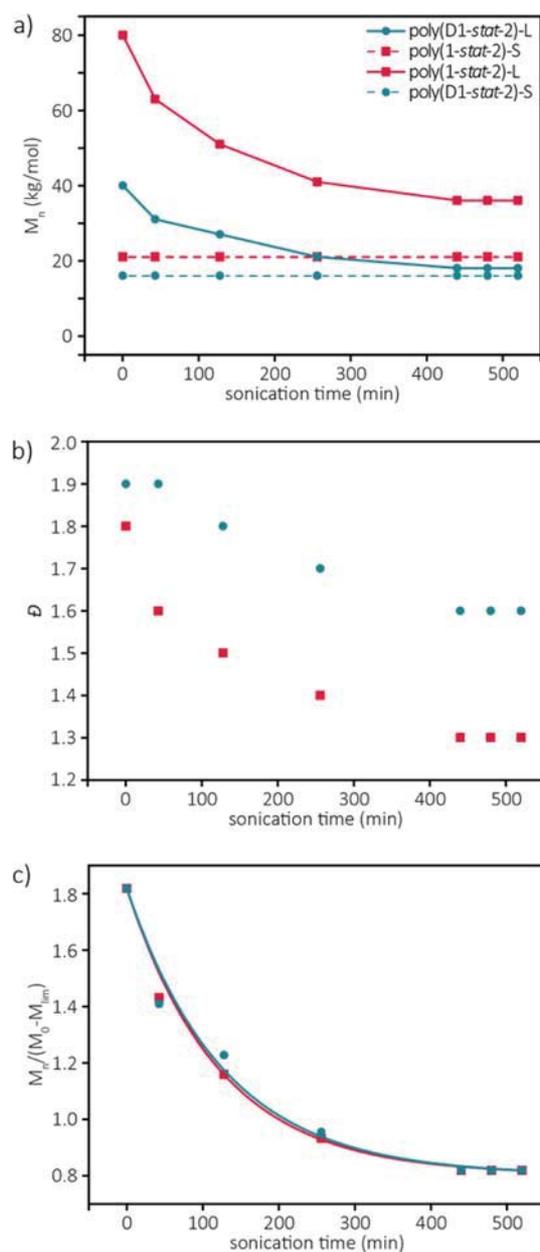


Figure 5. (a) Decrease of number-average molecular weight (M_n) as a function of sonication time for **poly(1-stat-2)-L** (red solid line), **poly(D1-stat-2)-L** (cyan solid line), **poly(1-stat-2)-S** (red dashed line), and **poly(D1-stat-2)-S** (cyan dashed line). M_{lim} for **poly(1-stat-2)-L** and **poly(D1-stat-2)-L** is 36 000 and 18 000 g/mol, respectively. (b) Narrowing of the dispersity over sonication time for **poly(1-stat-2)-L** (red squares) and **poly(D1-stat-2)-L** (cyan circles). (c) $M_n/(M_0 - M_{lim})$ a function of time for **poly(1-stat-2)-L** (red squares) and **poly(D1-stat-2)-L** (cyan circles) and exponential decay fits (lines following the color code). Assuming the chain scission follows first-order kinetics ($dM_n/dt = k(M_n - M_{lim})$), rate constants were determined to be 8.2×10^{-4} and $7.8 \times 10^{-4} \text{ min}^{-1}$ for **poly(1-stat-2)-L** and **poly(D1-stat-2)-L**, respectively.

This strategy allowed the demonstration that the original backbone and therefore the degree of polymerization were not altered. Additionally, the chain scission events could be modeled quite accurately using a mass balance equation. The present findings solve an important fundamental question in the field of mechanochemistry of polymers that could help design new experiments aimed at gaining a deeper understanding of stress transfers

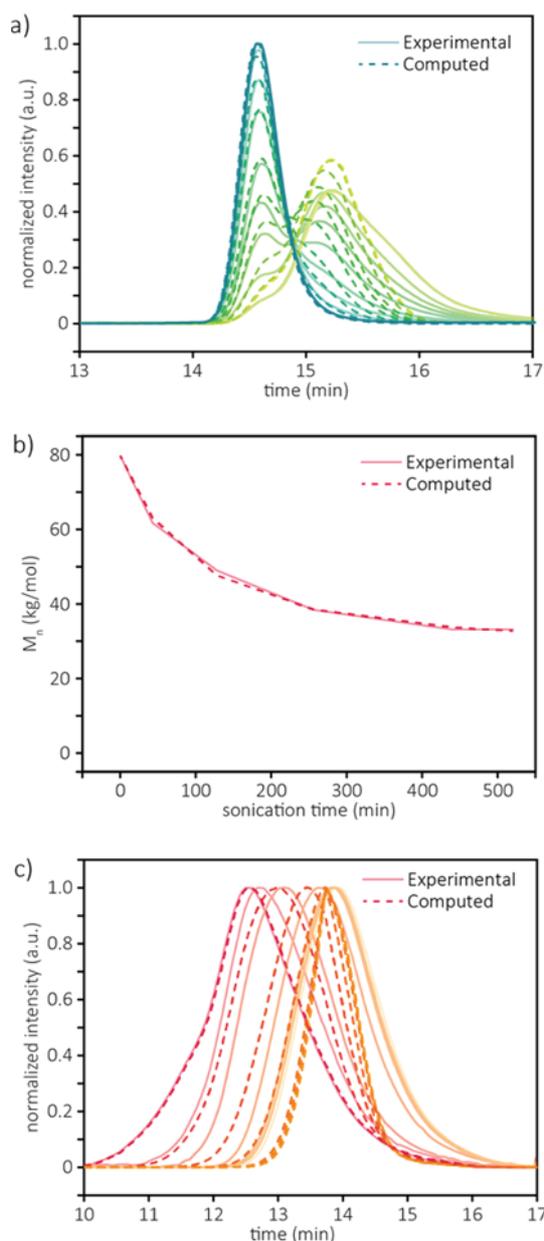


Figure 6. (a) Time evolution of the SECs (solid lines) for **PS-L** compared to model predictions (dashed lines). (b) Time evolution of M_n of **poly(1-stat-2)-L**. The dashed line is the model prediction with Supporting Information eq 1.14, and the solid line represents experimental values. (c) Time evolution of the size exclusion chromatograms (solid lines) for **poly(1-stat-2)-L** compared to model predictions (dashed lines).

in macromolecular chains. This topic is actually quite timely, and in fact, while this manuscript was being revised, a compelling study by Moore and co-workers with a completely different methacrylate system corroborating our findings was published.³⁷

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available

Experimental procedures, characterization of the products, degradation rate calculations, and details of the mathematical model (PDF)

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Notes

The authors declare no competing financial interest.

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