

Going with the Flow: Tunable Flow-Induced Polymer Mechanochemistry

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Mechanical forces can drive chemical transformations in polymers, directing reactions along otherwise inaccessible pathways, providing exciting possibilities for developing smart, responsive materials. The state-of-the-art test for solution-based polymer mechanochemistry development is ultrasonication. However, this does not accurately model the forces that will be applied during device fabrication using processes such as 3D printing or spray coating. Here, a step is taken toward predictably translating mechanochemistry from molecular design to manufacturing by demonstrating a highly controlled nozzle flow setup in which the shear forces being delivered are precisely tuned. The results show that solvent viscosity, fluid strain rate, and the nature of the breaking bond can be individually studied. Importantly, it is shown that the influence of each is different to that suggested by ultrasonication (altered quantity of chain breakage and critical polymer chain length). Significant development is presented in the understanding of polymer bond breakage during manufacturing flows to help guide design of active components that trigger on demand. Using an anthracene-based mechanophore, the triggering of a fluorescence turn-on is demonstrated through careful selection of the flow parameters. This work opens the avenue for programmed chemical transformations during inline manufacturing processes leading to tunable, heterogeneous final products from a single source material.

1. Introduction

Integrating force responsive molecules, known as mechanophores, into polymers has allowed the exploitation of force to drive chemical processes such as colorimetric changes,^[1–3] changes in luminescence,^[4–6] catalytic activity,^[7,8] cross-linking reactions,^[9–11] generation of reactive species,^[12] and unlocked access to otherwise inaccessible chemical pathways.^[13] Novel mechanophore designs have emerged through the rapid development in understanding of the fundamental chemistry and the influence of the chemical environment, polymer structure and the forces required to drive activation.^[14–16] In solution, ultrasonication is the most widely used method to study mechanochemistry.^[17,18] Microcavitation and bubble collapse impart solvodynamic shear forces inducing the coil-to-stretch transition of the polymer chain. This drives a velocity gradient along the polymer backbone, elongation and the build-up of tension along the

polymer chain, leading to events, such as chain scission^[14] or ring-opening,^[19] that deliver the new functionality. This is an idealized approach to testing mechanochemistry, as it imparts a repeating strain rate over a controlled volume, allowing effective activation by tuning the exposure time. However, in realistic industrial flows, materials are mostly exposed to a finite series of different strain rates as they are pumped through systems and flow through nozzles or constrictions, in for example injection molding, inkjet printing, extrusion or spray drying.^[17,20] The factors affecting polymer activation during sonication are complex and have been extensively investigated^[14,16,21] yet do not translate between reported experimental techniques. Recently, the onset of activation of spiropyran mechanophores incorporated in bulk systems was found to be dependent more on the network structure and the strain hardening physics than on the isolated molecular characteristics of the mechanophore.^[22,23] Thus, there are significant benefits to specifically studying a flow-based approach to mechanochemistry, such as the more rigorous scientific analysis inherent in a single-pass experiment, the more readily modelled flows and the relevance to a broader range of industrial applications. The difference in elongation processes between sonication and flow systems is highlighted in Figure 1.

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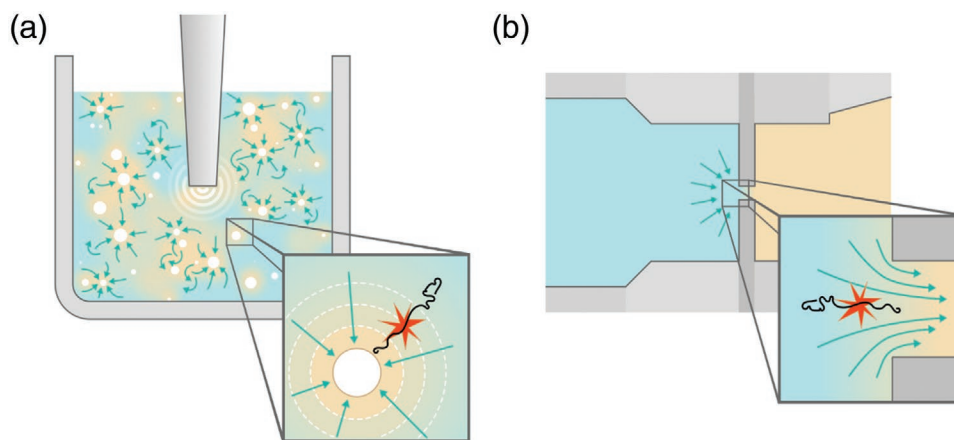


Figure 1. Schematic representation of a) probe sonication and b) the flow system described.

The degradation of polymers during different experimental flows is an established research area,^[24,25] however, these studies tend to focus on mechanical degradation rather than driving further chemical change and second, the flows examined do not scale to the macroscale laminar flows found practically within flow-based manufacturing processes. Long chain homopolymers are ubiquitous in such processes, including inkjet printing and electrospinning.^[17,26] Thus, the understanding of mechanical activation in polymeric systems in such scalable flows is vital, allowing the user to either protect the long chain molecule or drive mechanochemical change simply by tuning the process parameters. Mechanophores embedded within polymer materials have recently been used to distinguish between mechanical stimuli in the solid-state, activating to create colored radical species.^[27,28] A radical based colorimetric, force-dependent response is also possible in solution using the model system described here, adapted from a biological anti-oxidant assay. Mechanical activation of poly(methyl methacrylate) (PMMA), which is often used as the host polymer while designing novel mechanophores,^[14] proceeds via homolytic scission to produce two tertiary radicals.^[29] In this report, the colorimetric mechanochemical response of the model system is driven by reaction of these PMMA fragments with the radical trap 2,2'-diphenyl-1-picrylhydrazyl (DPPH). We chose this as the simplest and most rigorous model system of mechanochemistry that could be tested in a clean experimental approach, moving beyond pure polymer degradation toward controlled chemical reaction.

We aim, through the work here, to provide both fundamental insights into mechanochemistry under flow as well as a new and more controlled way forward for testing and benchmarking different molecular designs with a specific link to the most relevant industrial processes. Here, to take the first steps toward defining the parameters that control activation during flow, allowing it to be switched on or off, we compare the activation of our model chemical system via sonication to that of activation via a model flow through a nozzle or constriction. This flow is common to a wealth of industrial processes and allows us to test the roles of i) solvent viscosity and ii) fluid strain rate, while inclusion of a mechanophore at the center of the polymer chain also allows us to probe the role of iii)

the nature of the bond being activated and iv) the number of nozzle passes. Solvent viscosity, surface tension and vapor pressure all play a crucial role in the cavitation intensity produced during ultrasonication which in turn controls chain scission.^[30] However, the experimental flow system described here is dependent on shear alone and not cavitation, which makes it possible to decouple the contributions to cavitation and study, for example, the role of changing only the solvent viscosity or a targeted strain rate. Similarly, the lack of cavitation removes the possibility of intense localized heating that accompanies cavitation during sonication and is also noted during small molecule mechanochemistry via ball-milling. This exciting level of control over the material functionality at the point of processing enables applications, such as embedding strain sensors or regions of force-activated catalysts within pre-existing materials.^[4,5,7,8]

2. Results and Discussion

The physical data and the measured overlap concentrations for each of the polymer samples ($10\,000\text{--}2\,000\,000\text{ g}\cdot\text{mol}^{-1}$ sample names are based on polymer molecular weight, i.e., $10\text{--}2000\text{K}$) in ethyl acetate (EA) are reported in Table S1 and Figures S1 and S2 in the Supporting Information. EA was used as the solvent to ensure solubility of both the polymer and radical dye. To ensure build-up of tension along the polymer backbone is only due to solvent-polymer interactions and not polymer entanglement, all samples discussed (unless specified) were prepared at $1/3$ of the overlap concentration. Mechanical activation depends on the contour length and the number average degree of polymerization (X_n) rather than polymer molar mass (M_n), when comparing monomer units of the same average effective bond length.^[31,32] In this instance and comparable to the recent report by McFadden and Robb,^[2] we refer to samples using the polymer molecular weight (MW) for ease of identification as all chains are comprised of PMMA. The reaction between PMMA radicals and DPPH (Figure 2a) was followed by monitoring the DPPH absorption band at 517 nm which decreases changing the solution from its native purple to a pale yellow (Figure 2b). To understand in detail the distribution of molecular weights

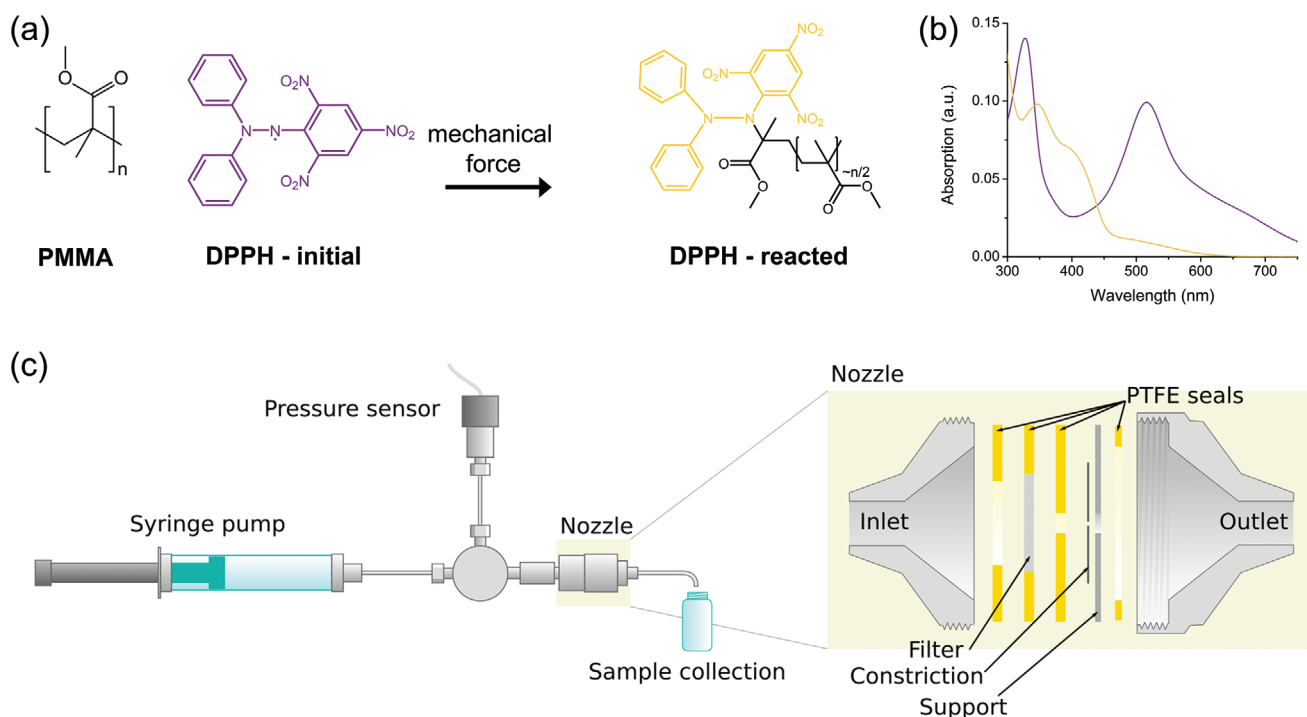


Figure 2. a) Structures of and reaction between poly(methyl methacrylate) (PMMA) and 2,2'-diphenyl-1-picrylhydrazyl (DPPH) following mechanochemical activation b) UV-vis absorption spectrum of native DPPH (purple line) and reacted (yellow line) in EA. c) Schematic of custom experimental flow system. Inset shows the construction of the nozzle constriction.

of the cleaved polymer chains, the solutions were also monitored via gel permeation chromatography (GPC). In this work DPPH was kept in excess and thus, the reaction rate between DPPH and PMMA is expected to be pseudo-first order and only dependent on the rate of mechanical chain scission of the PMMA chains.

2.1. Activation via Sonication

First, we tested our model system using ultrasonication as the standard mechanochemical activation process for dilute polymer solutions. These experiments were important to allow a comparison with our proposed new approach and so further details and discussion of these control ultrasonication experiments are outlined in the supporting information (Figures S3–S6, Supporting Information). Similar to trends expected from literature,^[14] it is shown that the rate of chain scission of this model system was dependent on the factors: polymer concentration, temperature and initial polymer chain length. It is worth noting that for ultrasonication in EA under our chosen conditions the limiting molecular weight, M_{lim} , below which no chain scission is observed, was found to be $\approx 223\,900\text{--}250\,000\text{ g}\cdot\text{mol}^{-1}$ through investigation of the effects of initial polymer MW and sonication time, respectively. This value is higher than that seen in the literature where chain scission is observed for polymers of the order of $\times 10^5\text{ g}\cdot\text{mol}^{-1}$.^[33,34] However, the sonication times used here are much shorter (3 min vs 1–2 h) coupled with the different solvent parameters of EA in which the polymer chains are not fully extended.

2.2. Activation via Flow Setup

The occurrence of mechanochemistry following ultrasonication is often cited as evidence that the same mechanochemistry will occur in the bulk phase.^[18] However, while this might be true qualitatively, it cannot give a quantitative indication of efficiency of this activation. Thus, the next step is to move our model chemical system into industrially relevant flows. We developed a customized fluid flow setup in which the fluid to be examined can be flowed in a highly controlled manner through a nozzle of known dimensions, see Figure 2c. A high-pressure syringe pump is used to push the fluid through a circular constriction at a specified volumetric flow rate. The deformation experienced by polymer chains as they pass the constriction is of elongational nature mainly, with a significant shearing component only close to the walls. This type of flow has been widely employed to study polymer elongation and scission, but its use in more advanced mechanochemistry application has remained very limited.^[25] The constriction itself is a laser-drilled hole in stainless steel foil, supported by a thicker metallic washer (further details of the setup and controls implemented are described in the Experimental Section and Figures S7 and S8 (Supporting Information)). The pressure upstream of the contraction is monitored to ensure steady-state flow and detect any obstruction. The maximum flow rate examined for PMMA in EA through the $25\text{ }\mu\text{m}$ diameter nozzle is 100 mL h^{-1} which gives rise to a wall shear rate in excess of $2 \times 10^7\text{ s}^{-1}$. For each of the fluid flow experiments, samples were taken prior to flow and after flow at the flow rate indicated.

At the highest achievable flow rate of the system, 100 mL·h⁻¹, for the 2000K sample, a small change in sample absorbance is observed, which equates to a 50.5% chain scission when measured via GPC, see Figure 3a,b. This is substantially lower than the 100% chain scission observed during the 3 min sonication time examined here. This is rationalized when considering the timescales and extensional events experienced during the two activation techniques. Cavitation during sonication takes place on the order of μs, thus a single polymer chain may experience upward of 1 million elongation events during 3 min of sonication. However, the exact number of elongation events a single chain experiences is extremely difficult to estimate not to mention difficult to control during sonication. In the flow setup, the shear and polymer elongation are limited to the flow through/into the constriction and thus allows superior control delivering a single extension and eventual chain breakage of the polymers examined. However, although macromolecules flowing along the same streamline experience the same macroscopic stress, the time taken for each molecule to be unraveled to a state where it is broken or activated is different depending on its initial random-coil configuration. Molecules which are already fairly straight and aligned with the elongation axis will break first and possibly break multiple times, while those having the worst kink configuration may not break at all, as examined by molecular dynamics simulations.^[35] In addition, the flow field itself is not homogeneous, leading to different stress history experi-

enced by molecules flowing along different streamlines. In particular, the velocity is lower close to the walls, providing a longer residence time compared to the centerline. These are contributing factors to the reduced chain breakage observed in the flow setup when compared with sonication (Figure 3c). Similar to ultrasonication, a trend is observed of increasing reaction with increasing initial polymer MW (Figure 3c). The % chain breakage for the maximum flow rate increases from 5% for 1000K to 27.1% for 1500K and to 50.5% for 2000K. It is also clear that the M_{lim} in EA is much higher in the nozzle system when compared to sonication, with no chain breakage observed for the 700K sample and lower MWs, see Table S2 in the Supporting Information. This difference in chain scission on moving from sonication to simple nozzle flow is analogous to the differing magnitude of mechanical activation observed in literature in the bulk phase when compared to that of dilute solution. This is due to the dominance of different effects on the polymer strain rate, which are explored further below. Unlike the complex environment of sonication, the parameters affecting polymer extension and breakage during fluid flow have been elegantly described in literature.

By modelling of linear polymers in fluid flows Keller and Odell have previously shown that the tension built up in the polymer backbone is proportional to i) solvent viscosity and ii) polymer strain rate as shown in Equation (1)^[36,37]

$$F \propto \eta_s \times \dot{\epsilon} \quad (1)$$

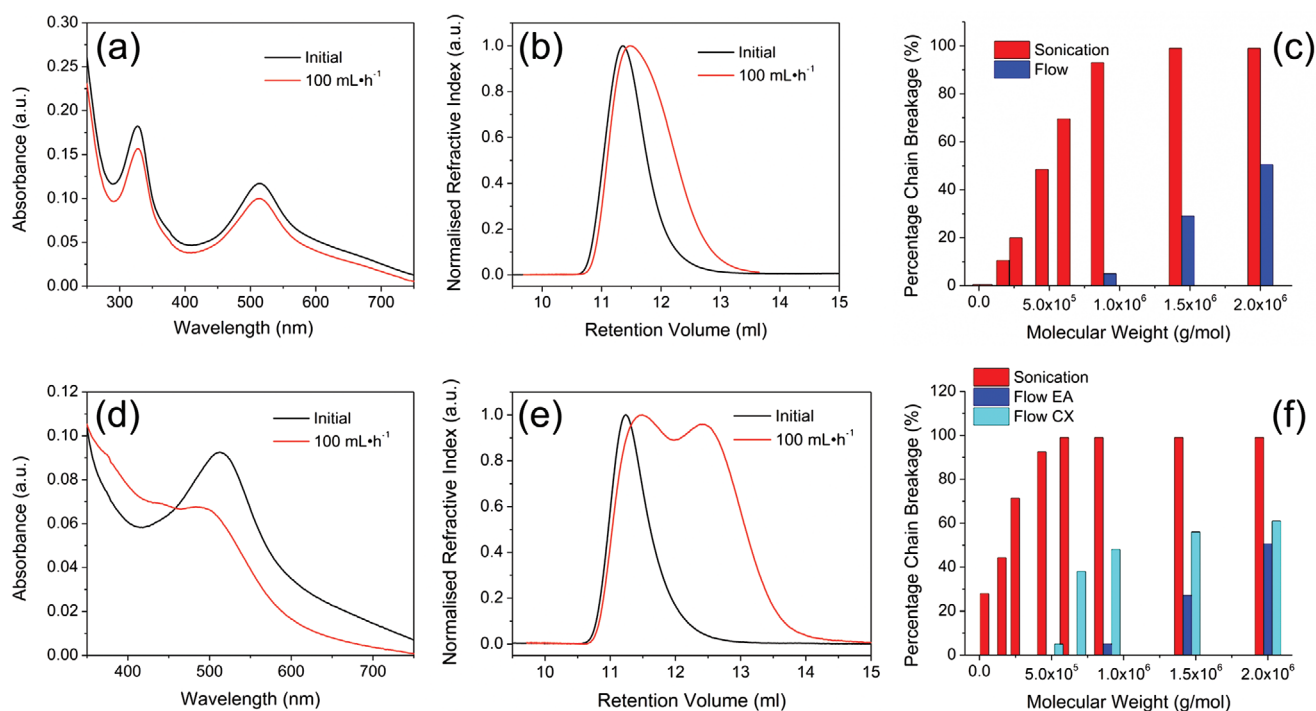


Figure 3. Mechanochemical activation of PMMA 2000K at 1/3 the overlap concentration in EA and CX in flow through a 25 μm nozzle a) UV-vis absorption spectrum in EA before (black) and after (red) flow at 100 mL·h⁻¹, b) GPC RI traces before (black) and after (red) flow at mL·h⁻¹ in EA and c) comparison of the percentage chain breakage as a function of initial MW measured via GPC for the sonication (red) and flow at the highest achievable flow rate of 100 mL·h⁻¹ (blue). d) UV-vis absorption in CX before (black) and after (red) flow at 100 mL·h⁻¹, e) GPC RI traces before (black) and after (red) flow at 100 mL·h⁻¹ in CX and f) comparison of the percentage chain breakage as a function of initial MW measured via GPC for the sonication in CX (red) and flow at the highest achievable flow rate of 100 mL·h⁻¹ in CX (cyan) and EA (blue).

where F is the tension in the backbone, η_s is the solvent viscosity and $\dot{\epsilon}$ is the polymer strain rate.

2.2.1. Increased Viscosity Leading to Increased Activation

Looking at the first of these parameters, solvent viscosity, it is possible to rationalize the reduced chain scission and reaction seen in EA in the flow system. EA is a very low viscosity solvent at 0.42 mPa s^[38] making it difficult to transfer the elongational stress directly to the polymer. It was hypothesized that this may be overcome by moving to a solvent with a higher viscosity. We chose cyclohexanone (CX) which has a surface tension of 34.4 mN m⁻¹ similar to that of EA (23.2 mN m⁻¹) but with a much higher viscosity of 2.01 mPa s. The physical data and the measured overlap concentrations for each of the samples in CX are reported in Table S3 and Figure S9 in the Supporting Information. The Mark-Houwink a parameter is a representation of how good a solvent is for a particular polymer. The similar a values suggests that CX (0.66) acts as a similarly good solvent for PMMA as EA (0.68), and so the viscosity noted here is the key difference.

With ultrasonication we see the same trends for PMMA in CX as was observed in EA (Figure S10, Supporting Information), in terms of increasing chain scission and reaction with DPPH with increasing initial MW. With a move to the flow system and using the highest flow rate of 100 mL h⁻¹, we see, as predicted, an increase in chain breakage and reaction in the more viscous CX solvent system. It should be noted however that the role of viscosity can only be qualitatively analysed in this case. Indeed, while trying to impose an overall similar stress field with two different viscosities and matching flow rates, the Reynolds numbers will be different for the two fluids, and therefore the details of the flow will be different. The decrease in the band at 517 nm in the UV-vis absorption spectrum and increase in growth of the lower MW species in CX for 2000K is shown as an example in Figure 3d,e. However, it is possible that CX can also undergo nucleophilic attack by the PMMA radicals created, causing an underestimation of the chain scission via UV-vis absorption (see Figure S11 in the Supporting Information for details). Thus, the UV-vis measurements are used to prove reaction with DPPH is possible, however, the percentage chain scission is calculated solely from the GPC measurements. We observe that the M_{lim} is lower when working in CX, with chain breakage and reaction observed for 700K and a small percentage for the 500K sample, as shown in Table S4 and Figure S12 in the Supporting Information.

2.2.2. Increased Fluid Strain Rate Leading to Increased Activation

As expected from Equation (1), the second parameter to vary is the fluid strain rate $\dot{\epsilon}$ which is controlled either by changing the nozzle dimension or the sample flow rate. For our experiments the nozzle diameter was fixed at 25 μ m. Thus, varying the flow rate allowed control over the chain scission and reaction. Increasing the flow rate from 60 to 80 and further to 100 mL h⁻¹ increased the percentage scission from 55 $\pm$ 2.9% to 58 $\pm$ 2.5% to 61 $\pm$ 2.6%, respectively, for the 2000K sample. For the higher molecular weight samples in particular this

trend is further highlighted by a shift to longer retention times and thus lower molecular weights for the peak corresponding to the broken polymer chains. The flow rates of 60, 80, and 100 mL h⁻¹ correspond to fluid extensional strain rates of 2.72×10^6 , 3.62×10^6 , and 4.53×10^6 s⁻¹, respectively. This is demonstrated by the growth of a lower MW species at longer retention times in the GPC traces for higher MW samples as shown in Figure S12 in the Supporting Information. In each case the percentage breakage is improved on that for EA at the same flow rates, Figure 3f shows the 100 mL h⁻¹ samples.

2.2.3. Reduced Bond Strength Leading to Increased Activation

There are clear design rules found from the work above on viscosity and strain rate, allowing much improved control and translation of mechanochemistry when modifying materials during processing. However, it is also critical to examine the role of the nature of the bond being activated. The force required to mechanically break C–C bonds, such as those found in the PMMA backbone, is ≥ 1 nN, whereas the forces required to break typical mechanophores lie in the range of ≈ 200 –2 nN.^[17] Thus, inclusion of a mechanophore within the polymer backbone will allow greater sensitivity toward activation within the flow system and allow us to explore the role of the chemical nature of the bond. Anthracene-maleimide cycloadducts have been used as mechanophores to probe mechanical activation at heterointerface,^[39,40] following micellar aggregation^[41] and to report chain rupture in polymer networks.^[42] The mechanophore used in this study, shown in Figure 4a, has previously been reported by Göstl et al.^[33,34] and was synthesized into the center portion of a long PMA chain 1. The GPC trace of 1 shows a major peak at 12.1 min attributed to the mechanophore-centered polymer 1 which also shows two shoulders, the high molar mass shoulder stems from bimolecular termination, the smaller low molar mass shoulder most likely stems from monofunctional initiation of the bifunctional, telechelic mechanophore initiator. Both shoulders combined constitute less than 10% peak area, and thus mass fraction, of the overall polymer and hence we hypothesize that this deviation has no significant impact on the sample activation. Ultrasonication of 1 is expected to proceed via a retro Diels–Alder reaction to produce a maleimide and a 9-phenylethynylanthracene terminated PMA fragment (Figure 4a). The overlap concentration of 1 was measured as 7.78 mg mL⁻¹. As before, starting with control experiments, ultrasonication of 1 in CX gave rise to the appearance of a well-defined band in the UV-vis spectrum at 400 nm indicative of the formation of the anthracene species.^[33] The GPC trace shows the disappearance of the high MW band at 12.1 min and the appearance of lower MW bands at 12.8 and 13.3 min as shown in Figure 4b,c. The first of these bands at 12.8 min is attributed to breakage of the polymer chains at the mechanically strained bonds in the mechanophore. While the second centered at 13.3 min is attributed to further non-mechanophore site specific chain breakage. The further quantification of mechanophore activation for 1 is carried out based on the change in UV-vis absorption observed following sonication as the complete disappearance of the

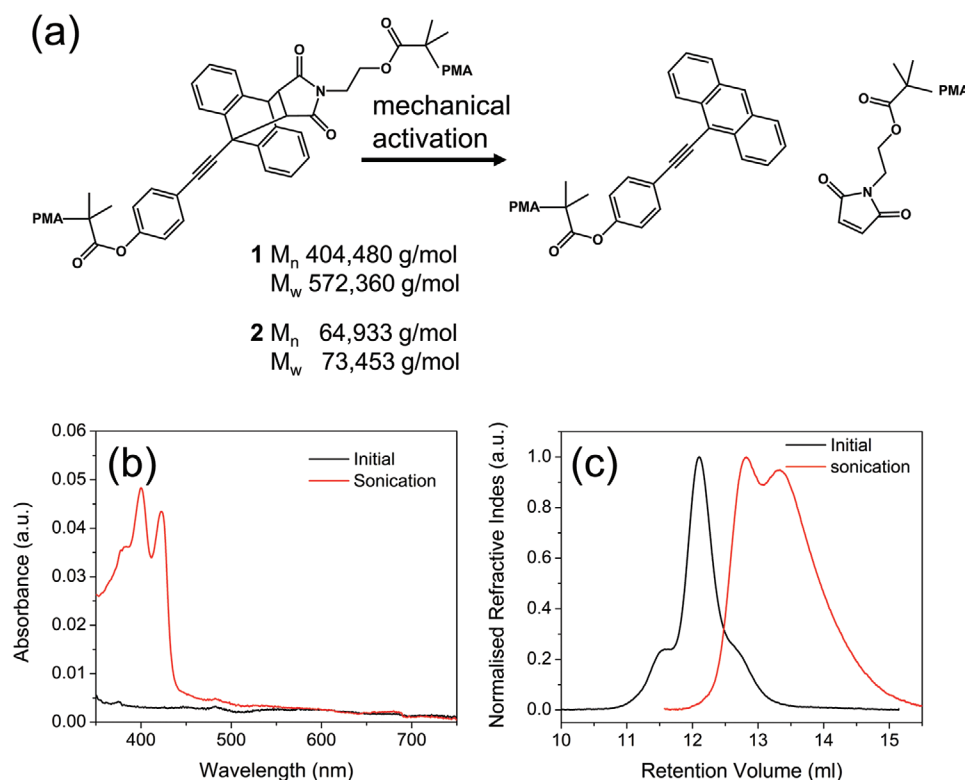


Figure 4. a) Structure of the mechanophore used which undergoes retro Diels–Alder (DA) reaction releasing a maleimide and a 9-phenylethynylantracene terminated PMA fragment. b) UV-vis absorption spectrum and c) GPC RI traces of **1** before (black) and after (red) sonication in CX.

mechanophore-centered peak at 12.1 min in the GPC trace suggests full mechanophore activation was achieved. The calculations for mechanophore quantification are detailed further in the supporting information.

This was explored further in the nozzle flow setup at a flow rate of $100 \text{ mL} \cdot \text{h}^{-1}$ and a decrease in the high MW shoulder in the GPC was observed with a concomitant growth in the lower MW band, along with an appearance of the anthracene band in the UV-vis absorption spectrum, see **Figure 5**. This corresponds to $\approx 23\%$ chain scission and activation of the embedded mechanophore species. Thus, the M_{lim} for the

mechanophore species is lower than $4.04 \times 10^5 \text{ g mol}^{-1}$, significantly below that expected of linear PMMA. As mentioned above, mechanical activation is dependent on chain length or degree of polymerization rather than MW. Considering the slightly lower MW of the PMA repeat unit, this $\approx 23\%$ activation is observed with a polymer with a degree of polymerization of 4758 compared to the linear PMMA samples in CX which showed $<5\%$ chain scission for the sample degree of polymerization of 4920 (PMMA500K). The inclusion of the mechanophore within the polymer chain lowers the observed M_{lim} . Once again the rate of mechanophore activation was

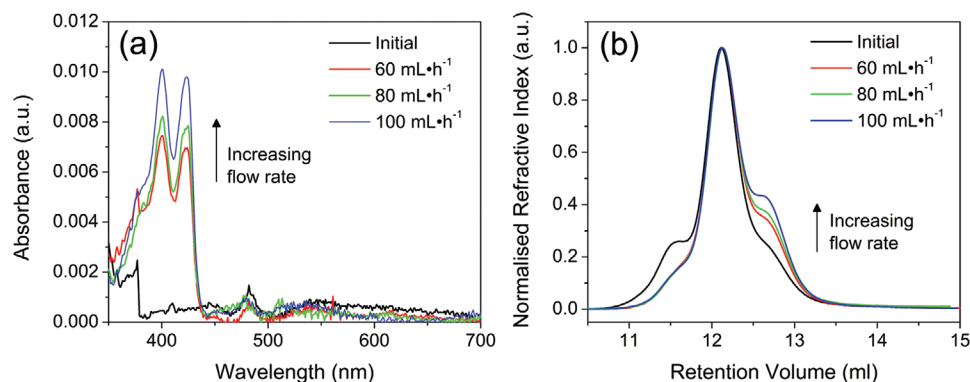


Figure 5. a) UV-vis absorption spectrum and b) GPC RI traces of **1** before (black) and after flow at 60 (red), 80 (green) and $100 \text{ mL} \cdot \text{h}^{-1}$ (blue) through a $25 \mu\text{m}$ nozzle in CX.

found to be controlled using the flow rate as also shown in Figure 5. As with the homopolymers discussed so far, as the concentration of the polymer is decreased there is an increase in mechanophore activation (Figure S13, Supporting Information). As a control, no mechanophore activation was observed for a much shorter chain polymer **2** ($M_n \approx 65 \text{ kg} \cdot \text{mol}^{-1}$) in CX during nozzle flow, while $\approx 5\%$ chain breakage was observed for **2** on sonication (Figure S14, Supporting Information). Similarly, no activation was observed for **1** dissolved in EA during nozzle flow compared to almost complete activation during sonication (Figure S15, Supporting Information). Once again, this highlights the contribution of solvent viscosity to the activation process.

2.2.4. Increased Number of Flow Passes Leading to Increased Activation

Using the flow setup, it is possible to control the number of possible elongational events a single polymer chain experiences during flow. Thus far, the measurements described have been single pass. However, it is possible to control the history experienced by the sample via multiple passes through the nozzle mimicking manufacturing process such as continuous inkjet (CIJ) in which the ink recirculates continuously. Increasing the number of times **1** passes through the $25 \mu\text{m}$ nozzle increases the absorbance at 400 nm in the UV-vis and causes a decrease in the high MW peaks at 11.6 and 12.1 min with growth of the lower MW band at 12.8 min as can be seen in Figure 6. This change is observable by eye through fluorescence when the samples are irradiated with UV-light as shown in the inset in Figure 6a. This equates to mechanophore activation of $\approx 25\%$, 41% , 64% , and 96% for 1, 2, 4, and 8 passes, respectively, almost matching the 100% achieved via 3 min sonication. In contrast with the sonication data, due to the more controlled nature of the flow setup, under the conditions examined, non-mechanophore specific chain scission does not occur as demonstrated by the lack of further lower MW peaks such as the peak observed at 13.3 min in the GPC following sonication.

3. Conclusion

In summary, it is clear that ultrasonication is indeed a good lab-based method to give the first level of confidence as to the operation of a mechanophore system. However, when moving to manufacturing relevant flows it is vital to understand specific quantitative aspects. Here, we have shown an experimental setup to provide quantitative analysis of chain breakage and subsequent reactions within manufacturing-relevant flows. For single-pass systems, we can see the role of solvent viscosity, sample flow rate, and through inclusion of a mechanophore we can understand the role of the activated bond in lowering the M_{lim} . This flow system simplifies experimental interpretation by avoiding cavitation-driven activation, allowing the decoupling of solvent parameters, such as solvent viscosity and vapor pressure, while also eliminating unwanted side processes that accompany cavitation, such as extreme localized heating. The control of polymer strain rate offered by the flow system described is a first important step to begin to build up the same level of detailed understanding of realistic flows that is currently available for ultrasonication. These results show that the move from destructive to productive polymer mechanophore chemistry within the chemistry lab has every possibility to scale to new materials and manufacturing flows. Large-scale processes using long chain polymers do not need to mitigate through trial and error for shear induced damage, but can instead choose the right flow and fluid parameters. Alternatively, they can pick from the developing literature in mechanophore design to use this chemistry and enhance their processes and material functionality.

4. Experimental Section

Materials: All reagents were obtained from commercial suppliers and used as received. Ethyl acetate (HPLC grade, $\geq 99\%$) was obtained from Fischer Scientific, UK. Cyclohexanone (ACS reagent grade, $\geq 99\%$) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were obtained from Sigma Aldrich, UK. Linear samples of poly(methyl methacrylate), PMMA, gel permeation chromatography (GPC) standards were purchased from Agilent. The

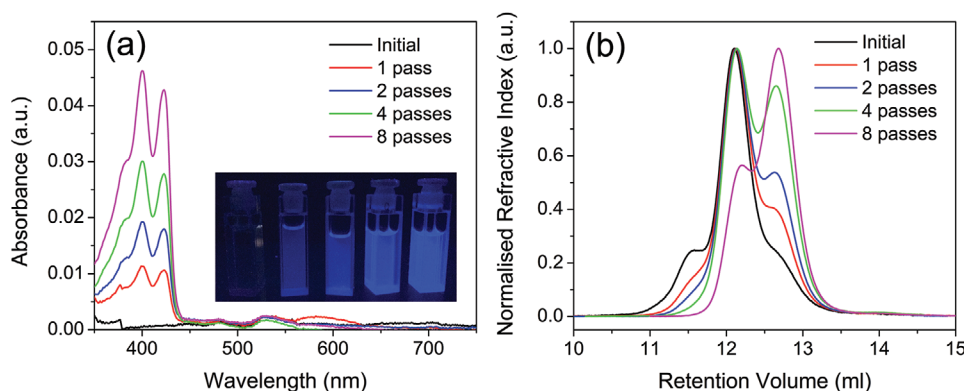


Figure 6. a) UV-vis absorption spectrum and b) GPC RI traces of **1** before (black) and after flow at $100 \text{ mL} \cdot \text{h}^{-1}$ for 1 pass (red), 2 passes (blue), 4 passes (green), and 8 passes (pink) through a $25 \mu\text{m}$ nozzle, Inset in (f): photograph of samples of **1** under UV-irradiation at 365 nm (left to right) initial, 1 pass, 2 passes, 4 passes, and 8 passes.

polymer sample name (based on nominal molecular weight), M_n and polydispersity index (PDI) are listed in Table S1 in the Supporting Information below. The Diels–Alder mechanophore 4-((13-(2-((2-Bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl-2-bromo-2-methylpropanoate and its corresponding polymers were synthesized according to literature procedures^[33,34] and briefly described in the Supporting Information.

Flow Setup: The liquid sample was initially drawn into a glass syringe (SGE Gas Tight). A syringe pump (KDS) pushes the sample inside a stainless steel fluidic system (Valco fittings), through a nozzle. The nozzle comprises a filter (Valco 2 micron stainless steel frit) and a constriction (Edmund Optics stainless steel 25 μm pinhole) and a stainless steel support washer. A SEM of the top view of this pinhole is shown in Figure S7 in the Supporting Information. The stack was held in place in a stainless steel filter holder and made liquid tight using custom made PTFE rings. A pressure sensor (Honeywell MLH series, wetted parts: stainless steel 304L and Haynes 214 alloy) was used to monitor the pressure upstream of the constriction. For each of the fluid flow experiments, samples were taken prior to flow and after flow at the flow rate indicated. A control was also taken for each sample at a slow flow rate of 10 $\text{mL}\cdot\text{h}^{-1}$ to ensure any chain breakage and reaction reported was only due to shear and elongation rather than any other interaction with the experimental setup.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fluid strain rate, manufacturing flow, mechanophores, nozzle flow, polymer mechanochemistry

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