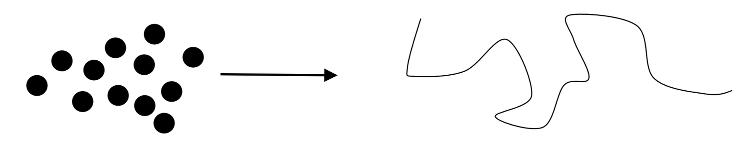
Mechanochemistry Probes Fundamental Polymer Physics

R. T. O'Neill and Prof. R. Boulatov,
Chemistry Department, University of Liverpool Crown St., Liverpool L69 7ZD, United Kingdom

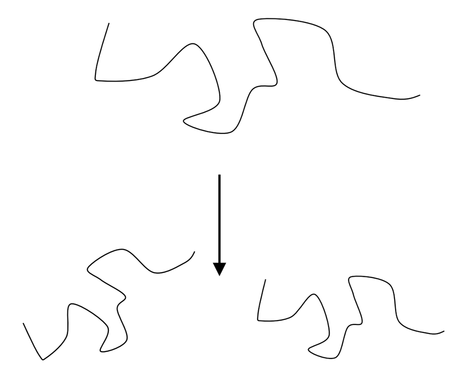
The century-old puzzle of polymer chain behaviour in complex flows.

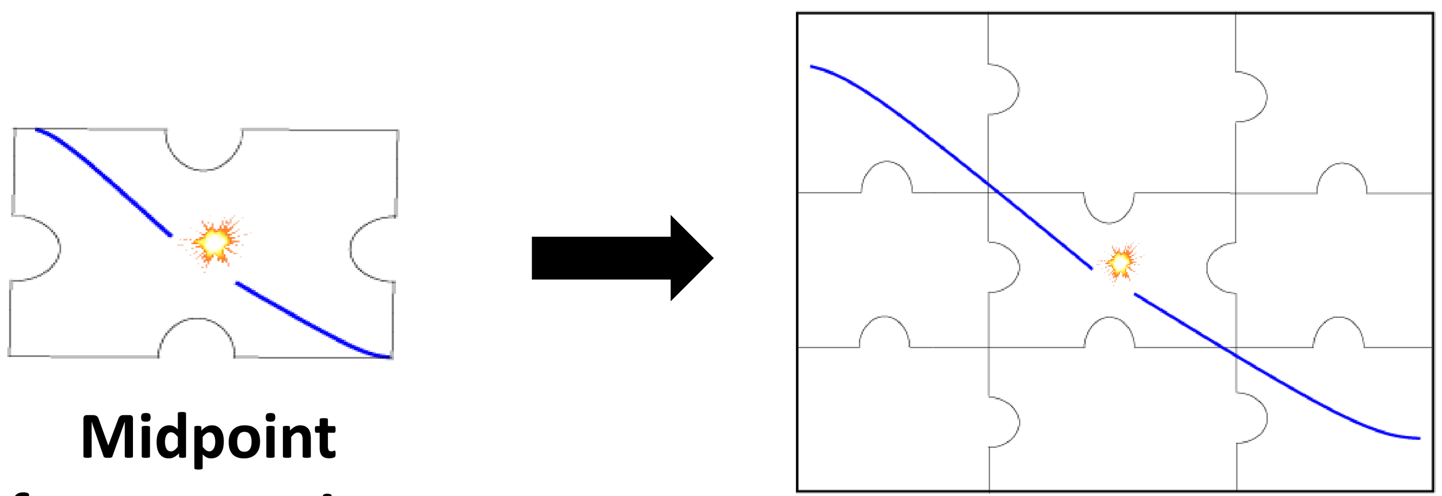
- Polymers are long chains of small repeating molecules, like **molecular strings**.



- Tiny amounts of polymer can drastically change the properties of liquids, allowing them to flow more easily. This has important industrial applications such as improving the efficiency of pipeline oil transport, but its effectiveness is limited by the fact that the **polymers break** when dissolved in these complex rapidly flowing liquids.

- The behaviour of polymer chains in these flows is **poorly understood** because there is no experimental set up that can directly visualise the polymers whilst they stretch and break. Instead, we infer how polymer chains behave from things we can observe such as the fact that the polymers break near their centre – like figuring out the whole jigsaw puzzle from just one piece.



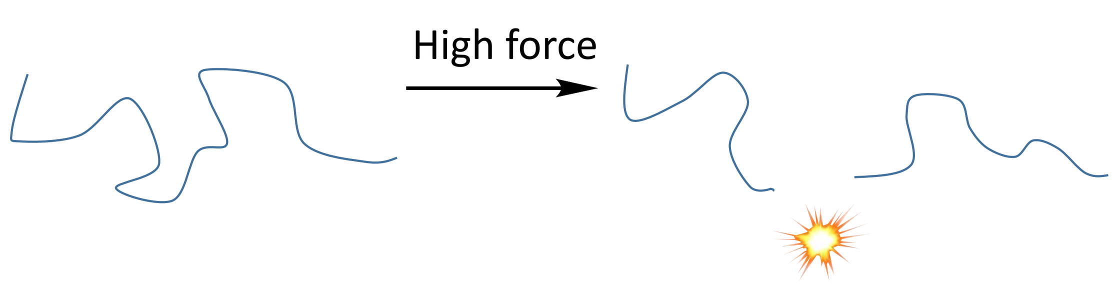


Midpoint fragmentation → **Fully extended chain model**

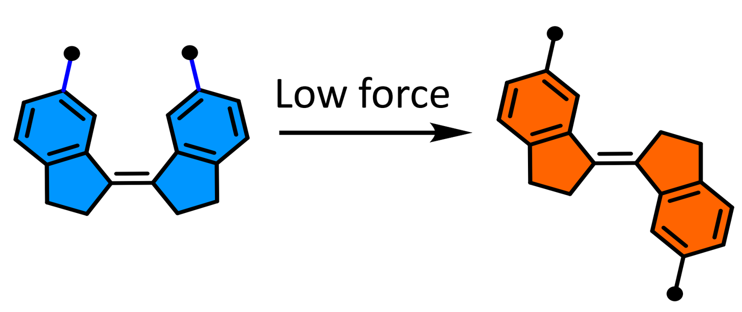
We needed **more detailed data** to 1) test if this model is correct or 2) refine it to improve our understanding of this fundamental polymer property.

Our approach uses mechanochemistry to test competing models.

Mechanochemistry refers to chemical reactions that occur when molecules experience **force**, such as the breaking of the chemical bonds in a polymer backbone when it is overstretched.

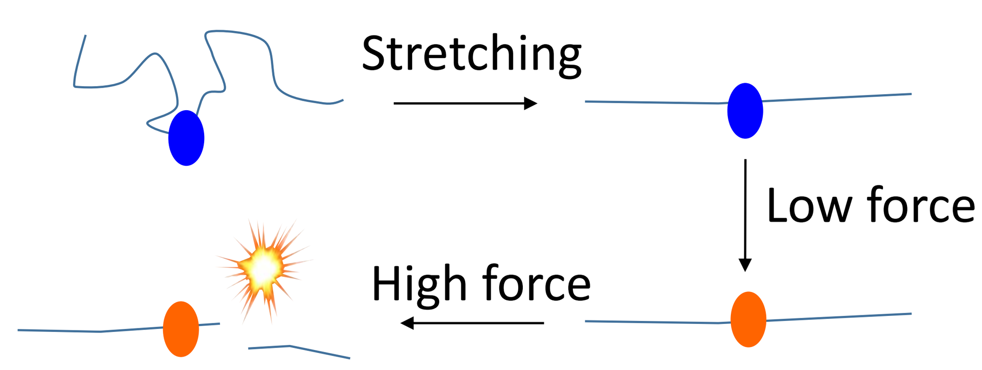


High force is required to break the **bonds** holding together the **polymer**.



Whereas a **much lower force** is required to change the shape (and colour!) of blue stiff stilbene.

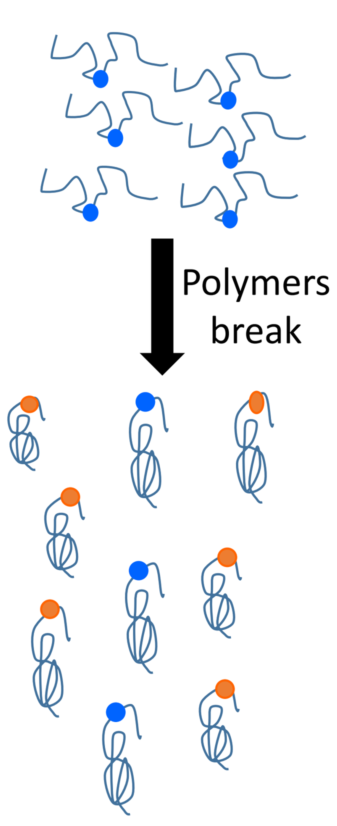
We **exploit this difference in force sensitivity** to test whether the chain is fully extended, if it is then a blue stilbene molecule in a polymer should **always** convert to orange before the chain breaks, since it occurs at much lower force.

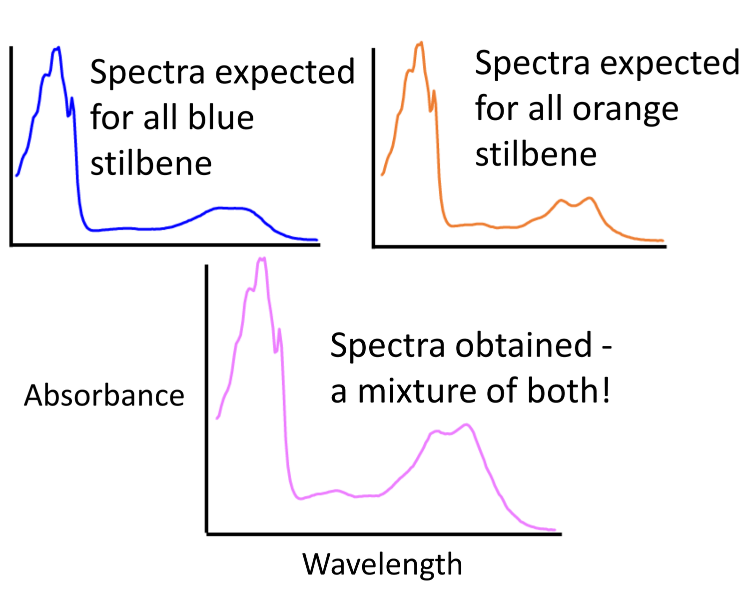


Results

We detect **significant amounts of blue stilbene** in broken chains, the **first experimental evidence** that chains are **not fully stretched** during complex elongational flows!

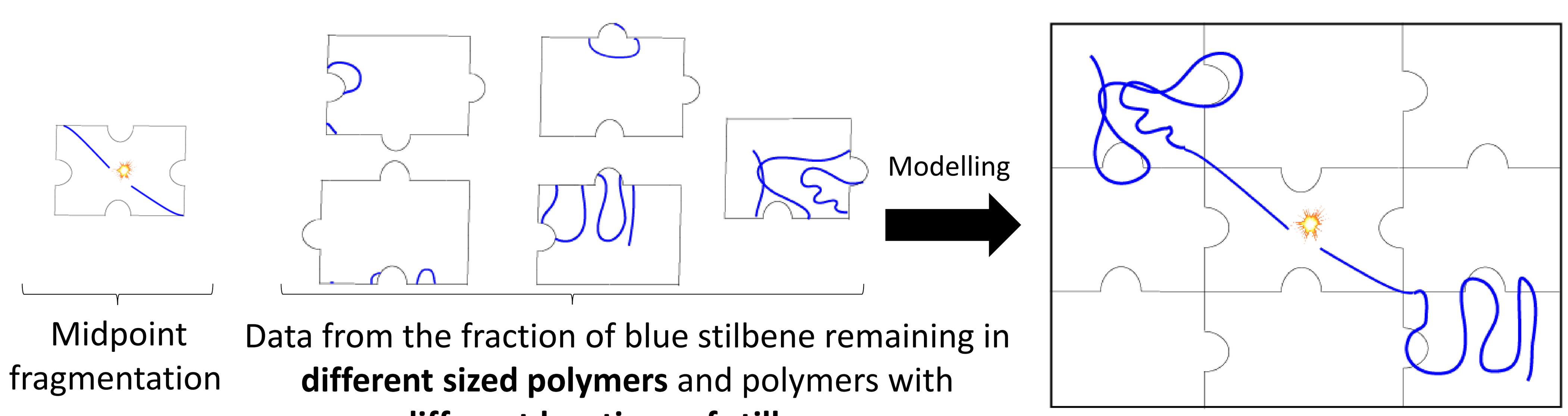
We obtain the ratio of blue to orange stilbene using Uv-Vis spectroscopy and fitting the measured spectra to reference data.





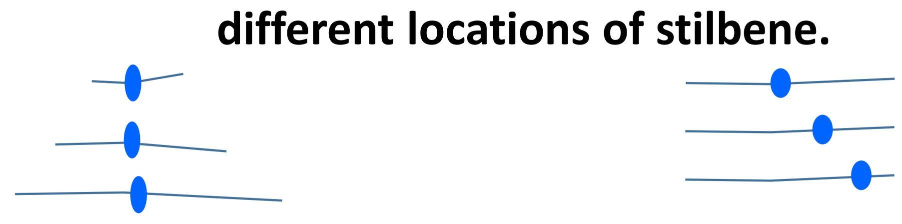
Our model

Informing our model with this much more detailed data than previously available yields an **unexpected insight** into this long standing problem.



Midpoint fragmentation

Data from the fraction of blue stilbene remaining in **different sized polymers** and polymers with **different locations of stilbene.**



Only **30%** of the polymer is stretched at breaking point!

Chains break whilst still partially coiled unlike any macroscopic object!

We hope this improved understanding of how polymers behave in complex flows, and more generally how they respond to applied force, allows better exploitation of their flow effects and the design of new force resistant smart materials.

Acknowledgements and References

We would like to thank the **University of Liverpool**, **EPSRC** and the **Royal Society** for funding this work.

- **O'Neill, R. Boulatov, R.** *The many flavours of mechanochemistry and its plausible conceptual underpinnings*, ***Nature Rev. Chem.***, (2021).
- **Boulatov, R. et al.** *Experimentally realized mechanochemistry distinct from force-accelerated dissociation of loaded bonds*, ***Science***, (2017).
- **S. Craig, et al.** *The role of polymer mechanochemistry in responsive materials and additive manufacturing*, ***Nature Rev. Mat.***, (2021).
- **Chu, S, et al.** *Single polymer dynamics in an elongational flow*, ***Science***, (**1997**)