Polymer Mechanochemistry

Literature

- M. K. Beyer, H. Clausen-Schaumann, *Chem. Rev*. **2005**, 105, 2921
- M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev*. **2009**, 109, 5755
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- K. M. Wiggins, J. N. Brantley, C. W. Bielawski, *Chem. Soc. Rev*. **2013**, 42, 7130
- J. N. Brantley, K. M. Wiggins, C. W. Bielawski, *Polym. Int*. **2013**, 62, 2
- Z. Huang, R. Boulatov, *Chem. Soc. Rev.* **2011**, 40, 2359

Outline

Mechanochemistry and polymer degradation

Force responsive materials

Applications

Making and Breaking Covalent Bonds

- Temperature
- Light
- Electrochemistry
- ….
- Mechanical forces => Mechanochemistry

Mechanochemistry harnesses mechanical forces to modulate chemical transformations

Mechanochemical Synthesis

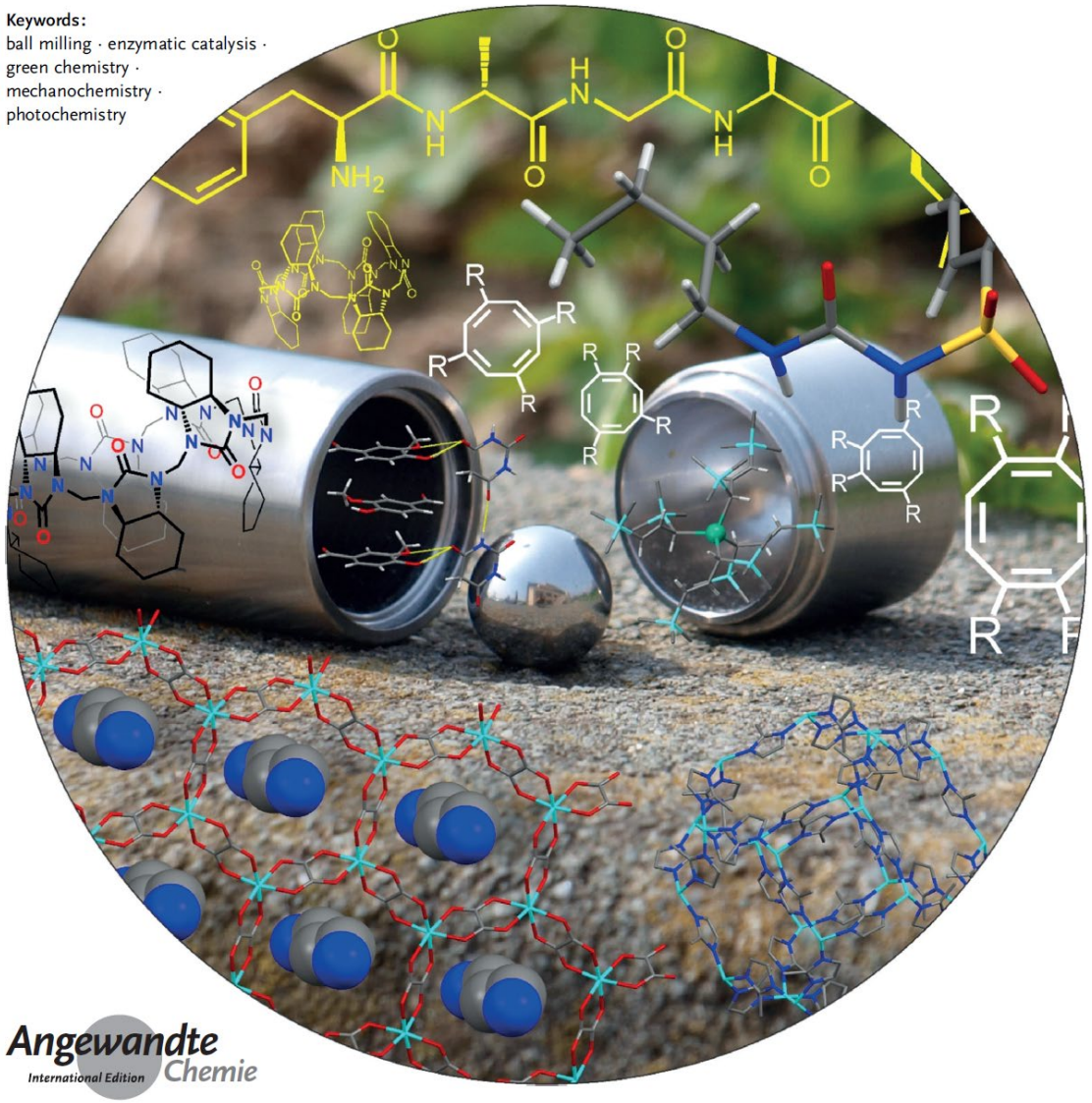


Image taken from: T. Friscic, C. Motillo, H. M. Titi, *Angew. Chem* **2019**, d.o.i. 10.1002/anie.201906755

Polymer Mechanochemistry

226. H. Staudinger und W. Heuer: Über hochpolymere Verbindungen, 93. Mitteil.[1]): Über das Zerreißen der Faden-Moleküle des Poly-styrols.

[Aus d. Chem. Universitäts-Laborat. Freiburg/Brsg.]

(Eingegangen am 14. Mai 1934.)

Tabelle 1: Mechanischer Abbau eines Poly-styrols vom Mol.-Gew. 470000.

Dauer d. Mahlung	Gd-mol. der Lösung	η_{sp} bei 20° in Tetralin	η_{sp}/c	Mol.-Gew.
0 Stdn.	0.005	0.427	85.4	470000
4 ,,	0.005	0.205	41.0	228000
8 ,,	0.005	0.105	21.0	117000
12 ,,	0.01	0.155	15.5	86000
16 ,,	0.025	0.221	8.84	49000
20 ,,	0.025	0.132	5.28	29400
24 ,,	0.05	0.174	3.48	19300
28 ,,	0.05	0.122	2.44	13600
32 ,,	0.05	0.109	2.18	12100
38 ,,	0.05	0.098	1.96	10900

H. Staudinger, W. Heuer, *Ber. Dtsch. Chem. Ges.* **1934,** *67,* 1159

Breaking Bonds in Polymers with Mechanical Forces

226. H. Staudinger und W. Heuer: Über hochpolymere Verbindungen, 93. Mitteil.[1]): Über das Zerreißen der Faden-Moleküle des Poly-styrols.

[Aus d. Chem. Universitäts-Laborat. Freiburg/Brsg.]

(Eingegangen am 14. Mai 1934.)

I. Über den Abbau von Faden-Molekülen im festen Zustand.

Der Kautschuk wird beim Mastizieren stark verändert, was sich darin äußert, daß die Viscosität seiner Lösungen danach erheblich niedriger ist als vorher. Früher führte man diese Veränderungen auf eine Desaggregation von Kautschuk-Teilchen zurück[2]). Ausgehend von ganz anderen Anschauungen über den Bau der Kolloidteilchen des Kautschuks[3]), wurde von dem einen von uns angenommen, daß diese Veränderungen bei der Mastikation auf einem Abbau der Makro-moleküle des Kautschuks durch Oxydation beruhen[4]). Die Änderungen, die der Kautschuk durch Mastikation erleidet, sind also nicht wie früher kolloid-physikalisch zu erklären[5]), sondern chemisch, da sie auf einer Verkleinerung der Kautschuk-Moleküle beruhen. Diese Angaben sind in letzter Zeit vielfach bestätigt worden, z. B. durch F. H. Cotton und andere[6]).

Nachdem jetzt erkannt wurde, daß die Moleküle des Kautschuks stab-förmige Gebilde sind, die sich etwa mit elastischen Glasfäden vergleichen lassen[7]), liegt die Vermutung nahe, daß beim Mastizieren neben dem Abbau der Moleküle durch Sauerstoff auch ein mechanisches Zerreißen der langen Faden-Moleküle stattfinden kann[8]). Wegen der enormen Sauerstoff-Empfindlichkeit des Kautschuks läßt sich aber nur schwer entscheiden, ob neben dem oxydativen Abbau auch ein mechanisches Zerreißen der Ketten beim Mastizieren stattfindet. Hierzu muß die Bearbeitung des Kautschuks unter strengstem Sauerstoff-Ausschluß durchgeführt werden[9]).

[1]) 92. Mitteil.: Cellulose-Chem. **15**, 53 [1934]. 91. Mitteil.: Helv. chim. Acta **17**, 335 [1934].

[2]) vergl. z. B. die Ausführungen von Wo. Ostwald: Welt der vernachlässigten Dimensionen, 9. u. 10. Aufl., S. 263 [1927]; ferner C. Harries, Kolloid-Ztschr. **33**, 181 [1923]; B. **56**, 1048 [1923]. Die Beobachtung von Klein u. Stamberger, Kolloid-Ztschr. **35**, 362 [1924], daß mastizierter Kautschuk im Gegensatz zu nicht mastiziertem ultramikroskopisch auflösbar ist, dürfte ihre Erklärung wohl in dem Hereinbringen von Verunreinigungen beim Mastizieren haben.

[3]) vergl. H. Staudinger u. J. Fritschi, Helv. chim. Acta **5**, 785 [1922].

[4]) H. Staudinger: Schweiz. Pat. 119027 vom 23. November 1925, ausgelegt 16. Februar 1927: Verfahren zur Mastizierung von Kautschuk dadurch gekennzeichnet, daß dieselbe unter Ausschluß von Sauerstoff vorgenommen wird.

[5]) vergl. z. B. die Ausführungen von C. Harries über die Plastizierung des Kautschuks, B. **56**, 1050 [1923].

[6]) F. H. Cotton, Transact. Rubber Ind. **6**, 501 [1931]; Fry u. Porrit, ebenda **3**, 203 [1927]; W. F. Busse, Industr. engineer. Chem. **24**, 140 [1932].

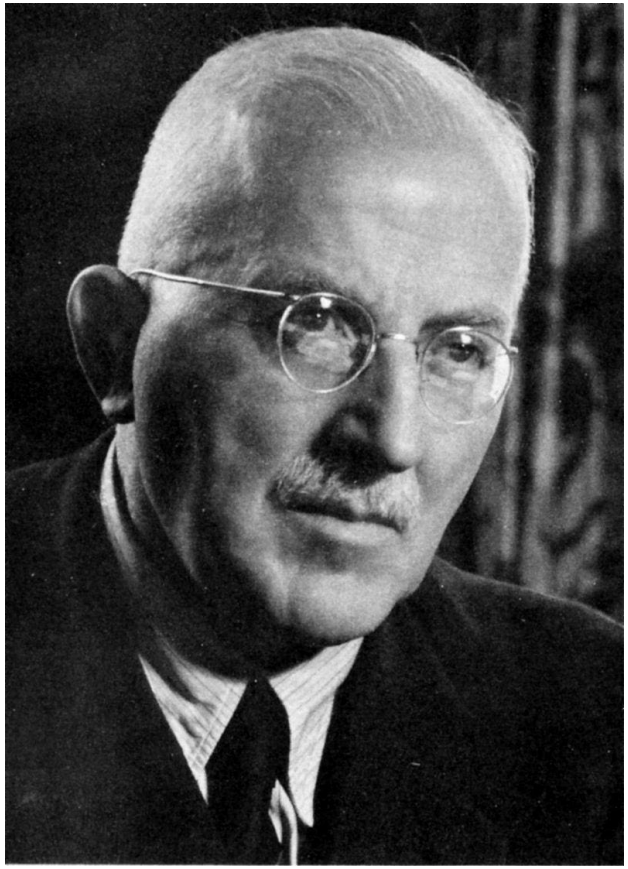
[7]) vergl. H. Staudinger, Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose (Verlag J. Springer, Berlin 1932), S. 79.

[8]) vergl. H. Staudinger, B. **63**, 926 [1930]; Van Rossem, Kolloidchem. Beihefte **10**, 129 [1919], ferner Bernstein, Kolloid-Ztschr. **12**, 193 [1913], führen die Veränderung beim Mastizieren auf eine Depolymerisation des Kautschuks zurück. Nur war damals der Begriff „Depolymerisation" noch nicht klar umschrieben.

[9]) Solche Mastizierungs-Versuche unter Luft-Ausschluß sind von Cotton, l. c., schon ausgeführt; aber es ist außerordentlich schwer, Kautschuk von Peroxyden vollständig zu trennen, und es ist immer zu beachten, daß nur sehr geringe Mengen von Sauerstoff notwendig sind, um einen Abbau der Kautschuk-Moleküle hervorzurufen; vergl. H. Staudinger u. E. O. Leupold, B. **63**, 730 [1930].

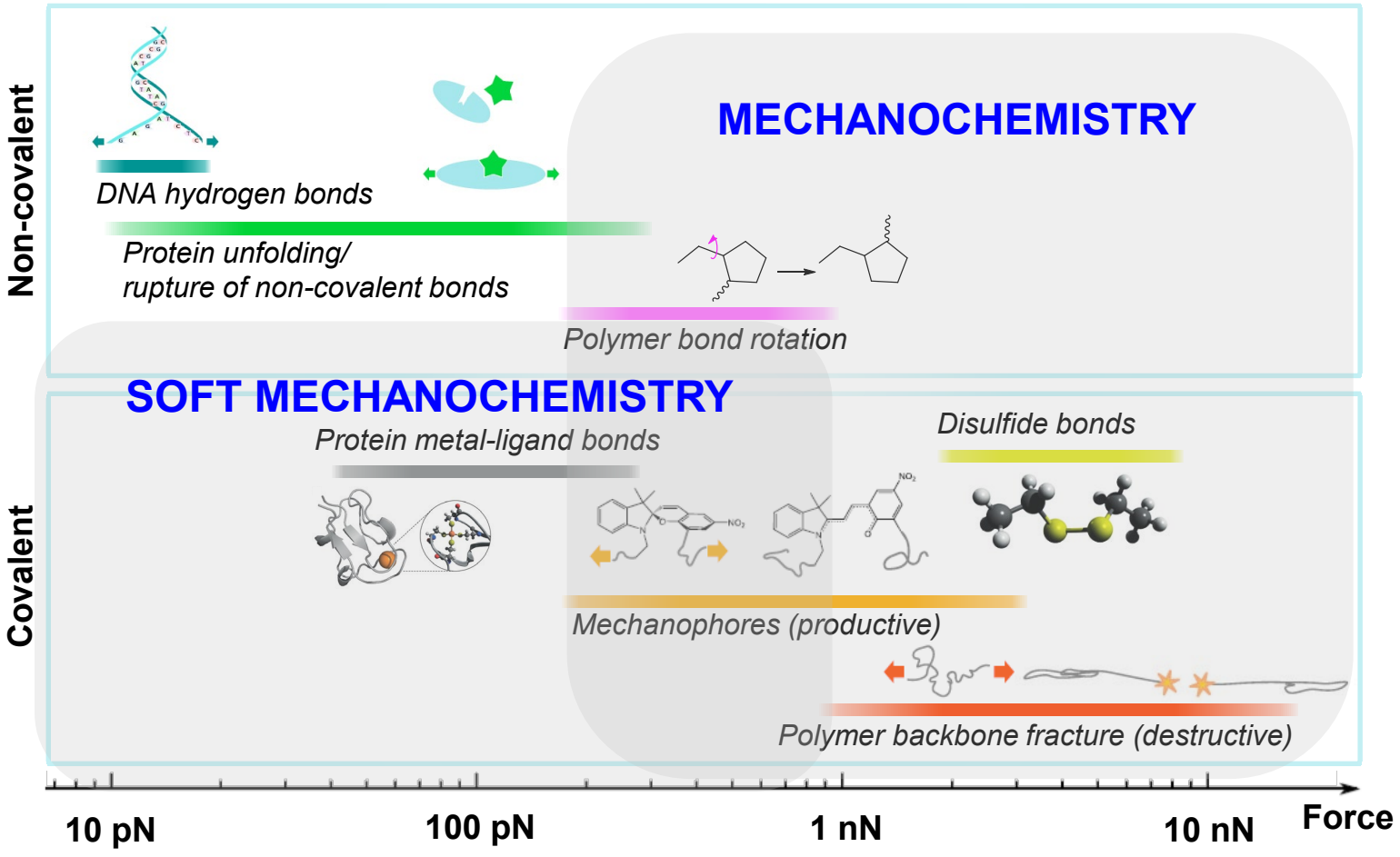
Introduction to Hermann Staudinger (1881-1965)

- Early work in understanding the response of polymeric materials to mechanical stress was published by Staudinger, who observed a decrease in the molecular weight of polymers in response to mastication (1930-1934)
- It was suggested that the molecular weight reduction resulted from homolytic carbon–carbon bond cleavage due to mechanical force
- 1953 Nobel Prize in Chemistry for demonstration of the existence of macromolecules



Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

(Bio)Polymer Mechanochemistry



Adapted from:

S. Garcia-Manyes, A. E. M. Beedle, *Nature Rev. Chem.* **2017**, *1*, 0083

N. Willis-Fox, E. Rogin, T. A. Aljohani, R. Daly, *Chem.* **2018**, *4*, 2499

From Non-Specific to Specific Bond Scission

ACCOUNTS of chemical research

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Polymer Mechanochemistry: From Destructive to Productive

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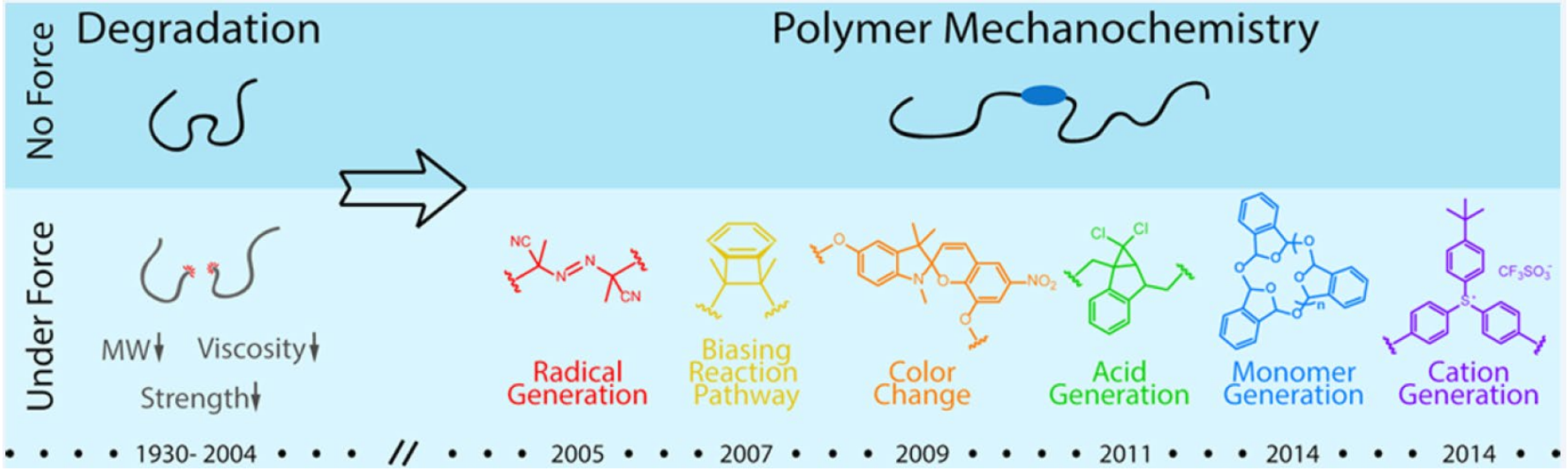
Beckman Institute for Advanced Science and Technology, Department of Materials Science and Engineering, Department of Chemistry, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States



Polymer mechanochemistry timeline

J. Li, C. Nagamani, J. S. Moore, *Acc. Chem. Res.* **2015**, *48*, 2181

Techniques to generate mechanical forces in molecules

Methods to Apply Mechanical Forces to Polymers

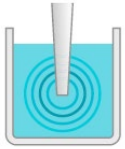
Method	Illustration	Typical conditions	Accessible strain rates	Maximum force
Flow fields (solution)		Dilute solutions (< 0.003 mg mL^{-1}); good solvent(s); high flow rates (> 10^4 s^{-1}); high molecular weight polymers (> 5 x 10^5 Da)	10^3-10^6 s^{-1}	10^{-10} N
Ultrasound (solution)		Dilute solutions (< 2.0 mg mL^{-1}); polar solvent(s) with low viscosities; applied intensity of 9-12 W cm^{-2}; high molecular weight polymers (> 6 x 10^4 Da)	10^6-10^7 s^{-1}	10^{-9} N
Manual elongation (solid-state)		Polymer film or mold is manually stretched or bend	~1 s^{-1}	~10^2 N
Tensile testing instrument (solid-state)		Polymer film or mold; moderate force is used (~1 N); low strain rate (< 1 s^{-1})	0-2 x 10^2 s^{-1}	10^5 N
Pressure cells (solid-state)		Unprocessed polymer; moderate force is used (< 8 x 10^2 N)	0-2 x 10^2 s^{-1}	10^5 N
Hydraulic presses (solid-state)		Unprocessed polymer; moderate force is used (< 2 x 10^2 N)	0-2 x 10^2 s^{-1}	10^5 N

Table adapted from:

K. M. Wiggins, J. N. Brantley, C. W. Bielawski, *Chem. Soc. Rev.* **2013**, *42*, 7130
N. Willis-Fox, E. Rogin, T. A. Aljohani, R. Daly, *Chem.* **2018**, *4*, 2499

Flow-Induced Mechanochemistry of Polymers in Solution

Elongational Field

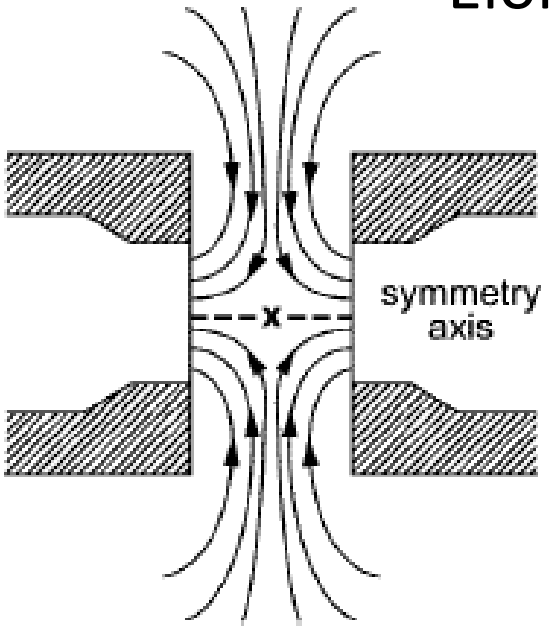


Figure 8. Opposite-jet flow cell. A schematic illustration of the flow pattern where the lines represent solvent velocity contours and the x represents the stagnation point.

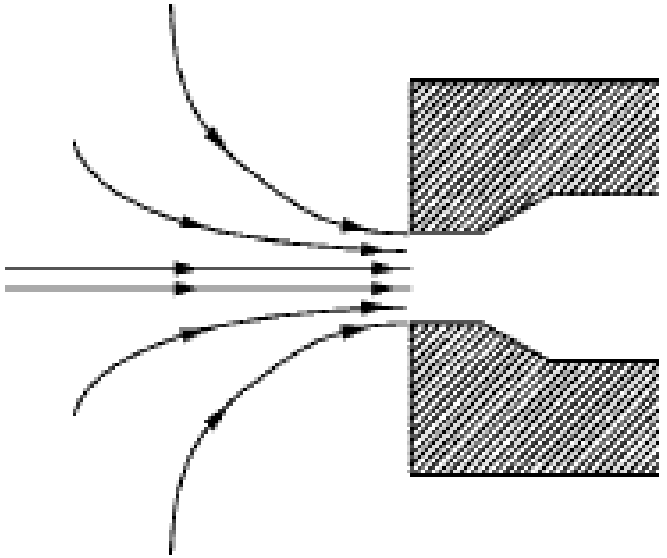
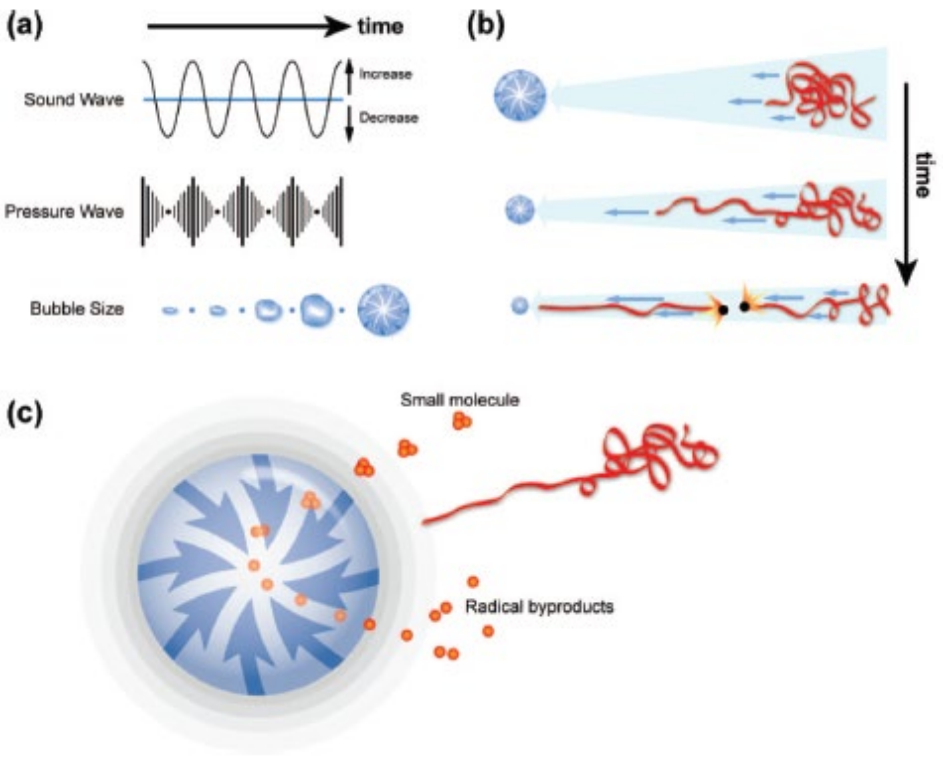


Figure 9. Constriction flow cell for transient elongational flow.

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Ultrasound-induced Chain Scission



Polymer segments in the high-gradient shear field near the collapsing bubble move at a higher velocity than those segments further away from the collapsing cavity. This velocity gradient causes the polymer chain to become elongated, and tension develops along the backbone of the polymer, which finally leads to chain scission.

Figure 12. Mechanism for ultrasound-induced polymer chain scission: (a) gradual bubble formation results from pressure variations induced by the acoustic field; (b) rapid bubble collapse generates solvodynamic shear; (c) small molecules undergo pyrolytic cleavage to form radical byproducts upon bubble collapse, while polymer chains do not undergo pyrolytic cleavage because they do not penetrate the bubble interface.

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

General Features of Ultrasound-Induced Polymer Chain Scission: Chain-Length Dependence and M_{lim}

Polymer chain scission occurs more rapidly for polymers with higher molecular weights. Chain scission ceases as the polymer chain length approaches a lower limiting value, M_{lim}. Below the M_{lim}, the polymer chain is too short to experience the forces required for bond cleavage. The molecular-weight

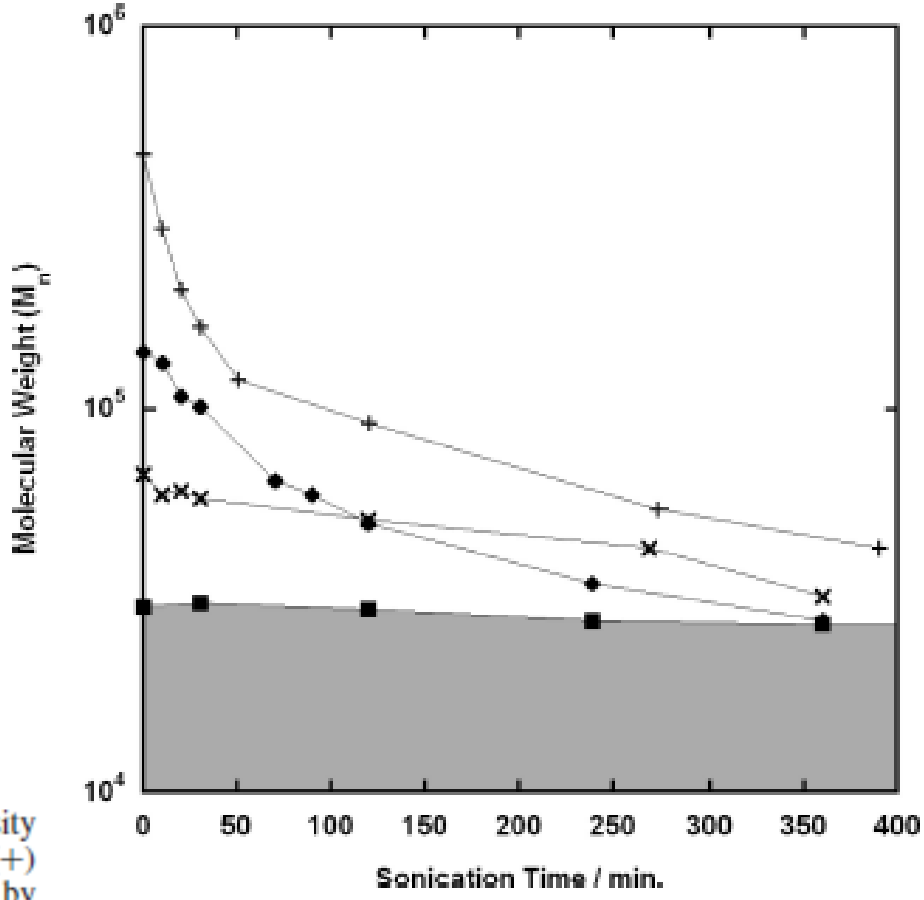


Figure 16. Ultrasonic chain scission of narrow polydispersity polystyrene in toluene: (■) 30,000; (×) 68,000; (◆) 140,000; (+) 460,000.[185] The limiting molecular weight, M_{lim}, is represented by the shaded region. (Experimental conditions: 50 cm^3 of 0.5 wt % solution irradiated at $I = 17.4$ W cm^{-2} at 25 °C).

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Kinetics of Chain Degradation

J. MACROMOL. SCI.–CHEM., A23(6), pp. 729-748 (1986)

Ultrasonic Solution Degradations of Poly(Alkyl Methacrylates)

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Mississauga, Ontario L5L1J9, Canada

Rate Constants

The relation [41, 42] between $\overline{DP}_n$ and time t in a random degradation process is given by

$$-\ln(1 - 1/\overline{DP}_{n,t}) = kt - \ln(1 - 1/\overline{DP}_{n,0}), \quad (3)$$

where $\overline{DP}_{n,t}$ and $\overline{DP}_{n,0}$ are the number-average degrees of polymerization at t = t and t = 0, respectively, and k is the rate constant.

According to Sato and Nelepa [43], Eq. (3) can be transformed to

$$\frac{1}{\overline{M}_{n,t}} = \frac{1}{\overline{M}_{n,0}} + k't, \quad (4)$$

where $k' = k/M_0$, and M_0 is the molecular weight of the monomer unit. Plots of $1/\overline{M}_n$ versus t will give k', and consequently k (Table 4).

Ultrasound Intensity

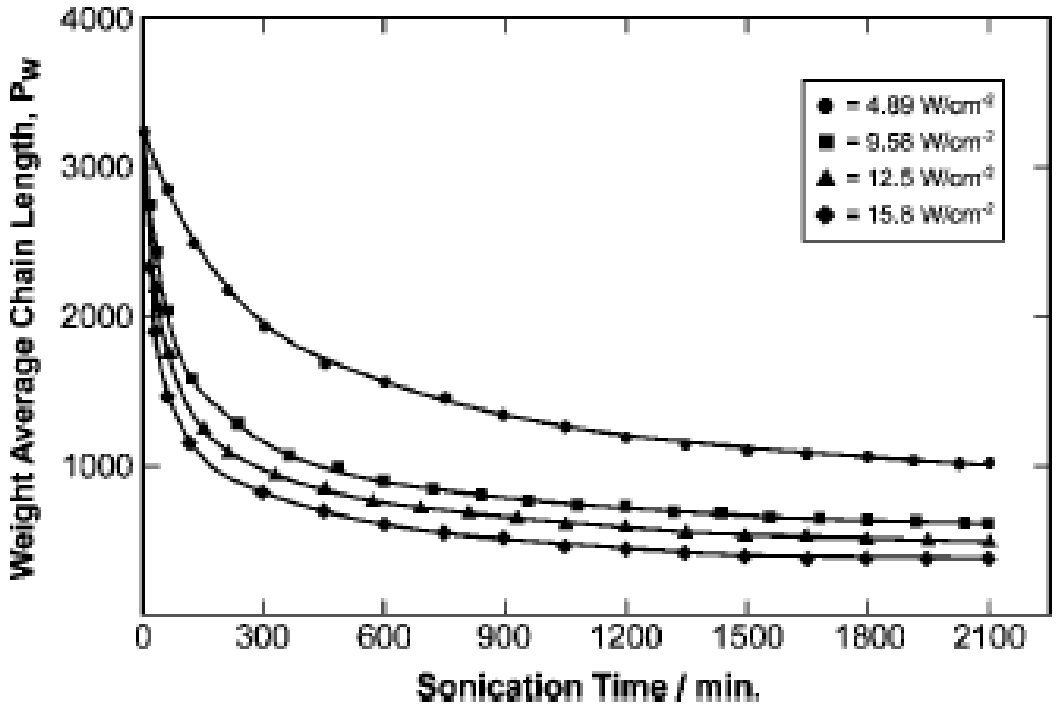

Figure 17. Effect of ultrasonic intensity on the chain scission of 25 mL samples of polystyrene in benzene (1 wt/vol %). Plot of chain length vs time in minutes for various ultrasonic intensities: (●) 4.89 W cm^{-2}; (■) 9.58 W cm^{-2}; (▲) 12.5 W cm^{-2}; (◆) 15.8 W cm^{-2}.[186]

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Effect of Solvent

Solvent plays a crucial role for ultrasound-induced polymer mechanochemistry.[175,190−198] Vapor pressure is the most influential solvent factor affecting the process. Other solvent properties, such as viscosity, surface tension, and the nature of the polymer−solvent interactions, can also influence the rate of ultrasound activation. The nature of the polymer−solvent interactions modulates the chain's equilibrium "coil size" prior to activation, with more miscible solvents facilitating the coil−stretch transition (refer to Figure 10).[118,150,167−170]

The effect of solvent vapor pressure is believed to influence the magnitude of shear forces generated upon the collapse of bubbles. Solvents with higher vapor pressures are more volatile, and as a result, more solvent vapor will enter the bubbles. This difference provides a cushioning effect on the collapse of the bubbles. The solvent movement is thus slower, and the shear stress exerted on the polymer chain segments is lowered, thereby leading to lower chain scission rates.

Compared to the effect of solvent vapor pressure on the rate of chain scission, the effect of the solvent viscosity is not as significant.[193,196,202,203] Increasing the solution viscosity typically leads to a decrease in the rates of chain scission. In more viscous solutions, an increase in viscosity raises the cavitation threshold. The hydrodynamic shear forces resulting from the bubble collapse are decreased. Furthermore, a polymer chain in a more viscous solvent is less flexible and moves more slowly toward the collapsing bubbles.

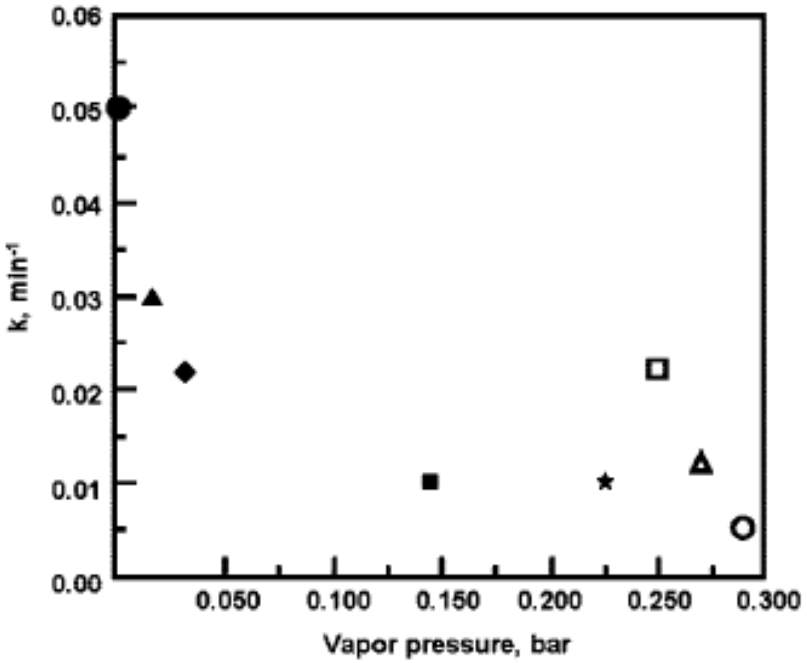

Figure 19. Effect of vapor pressure on the chain scission rate coefficient, k (min^{-1}), of poly(vinyl acetate) at a concentration of 2 g/L: ●, *o*-dichlorobenzene; ▲, chlorobenzene; ■, benzene; ◆, toluene; ★, chloroform. Model predictions: ○, acetone; △, 9:1 acetone/water; □, 4:1 acetone/water (ratios by volume).[194]

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Effect of Temperature

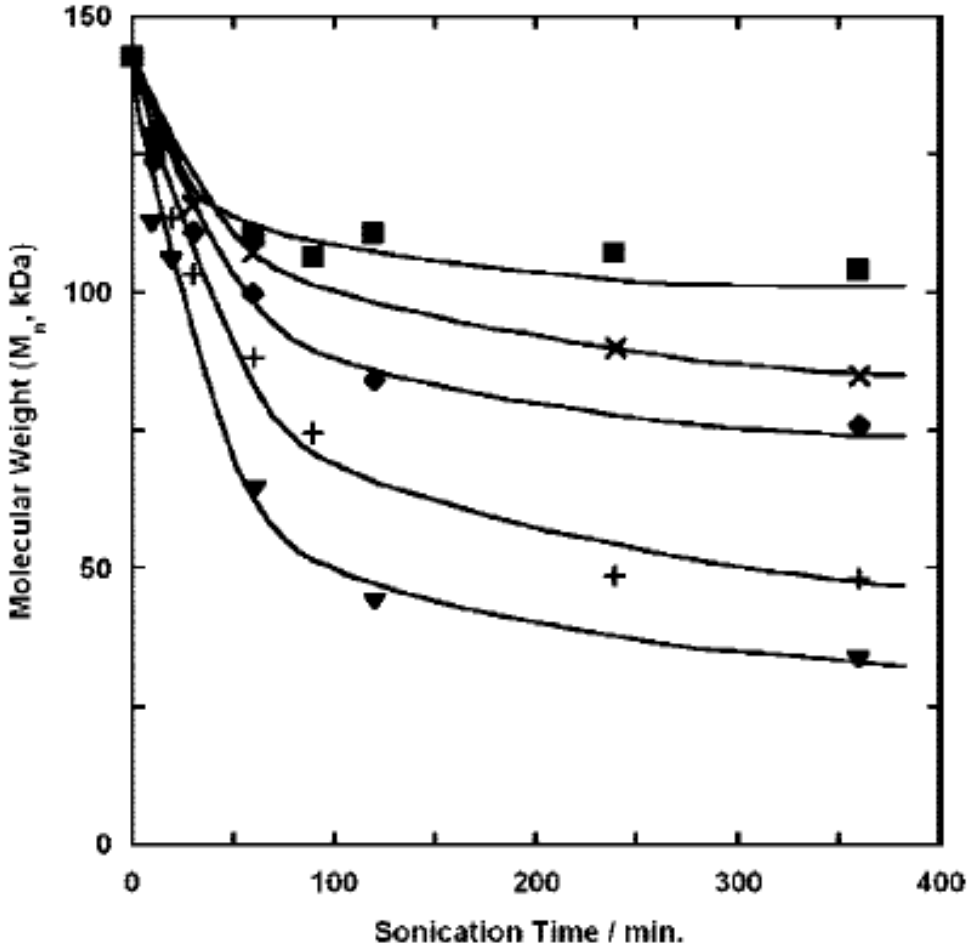


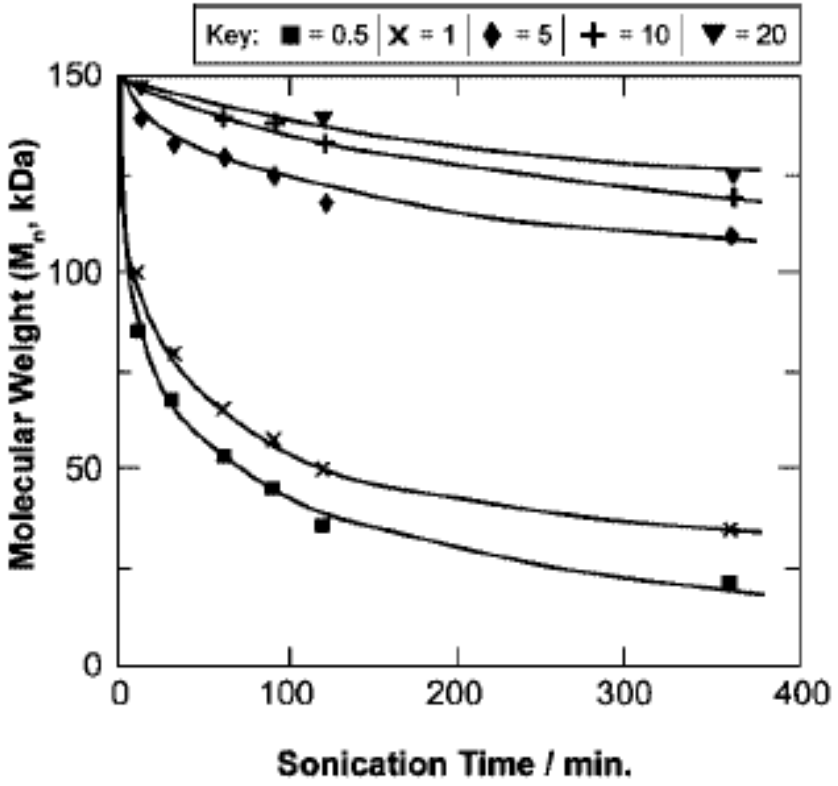
Figure 20. Ultrasonic chain scission of polystyrene in toluene at different temperatures: ■, 61 °C; ×, 50 °C; ◆, 40 °C; +, 5 °C; ▼, −10 °C (Experimental conditions: 50 cm^3 of 0.5 wt % solution irradiated at $I = 17.4$ W cm^{-2} at 25 °C).[185]

The majority of chemical processes are accelerated by an increase in temperature. However, the opposite effect is typically observed for the ultrasonic chain scission of polymers in solution. The chain scission rate decreases with increasing temperature (Figure 20).[185,195,204−207] This negative temperature coefficient has been observed for the ultrasonic chain scission of polystyrene,[185] poly(alkyl methacrylate),[195] poly(vinyl chloride), and poly(vinyl acetate).[208] In contrast, Yen and Yang reported that an increase in temperature increases the chain scission rate coefficient for the ultrasonic chain scission of polyacrylamide in water.[209] The negative temperature coefficient has often been cited as evidence that ultrasound-induced polymer chain scission is mechanical in origin.

The effect of temperature is attributed to changes in the physical state of the system, such as the vapor pressure and the viscosity of the solvent. At increased temperatures, the solvent pressure is higher, and a larger quantity of the solvent vapor enters the cavitation bubbles during expansion. As mentioned previously, this change exerts a "cushioning" effect during the bubble collapse. The intensity of the shear forces is lessened, and the solvent velocity is reduced. Consequently, the chain scission rate is decreased.

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Polymer Concentration Dependence



These observations are explained in terms of viscosity changes for different polymer concentrations. At higher concentrations, the solution viscosity increases. An increase in viscosity raises the cavitation threshold. This increased threshold makes it more difficult for cavitation bubbles to form. More importantly, the velocity gradients around collapsing bubbles become smaller, and the elongation of the polymer backbone is reduced.

Price noticed a large jump in the scission rate of polystyrene from polymer concentrations of 1% and 5% solution in toluene. The significant differences are attributed to the critical overlap concentration, C^*, the concentration at which chains begin to entangle. When chains begin to overlap, their movement and cleavage are more restricted, and chain recombination is more likely. Hence, the extent of chain scission is reduced. The critical overlap concentration in good solvents is estimated as 2.4 wt/vol % for polystyrene with molecular weight 448 kDa. This value matched the large difference observed for the chain scission rate between 1% and 5% polystyrene solutions (Figure 21).[196]

Figure 21. Chain scission of polystyrene in toluene at 25 °C at various concentrations (wt/vol %); the critical overlap concentration, C^*, was estimated to be 2.4 wt/vol %.[196]

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

From Polymer Degradation To Force Responsive Materials

Introduction

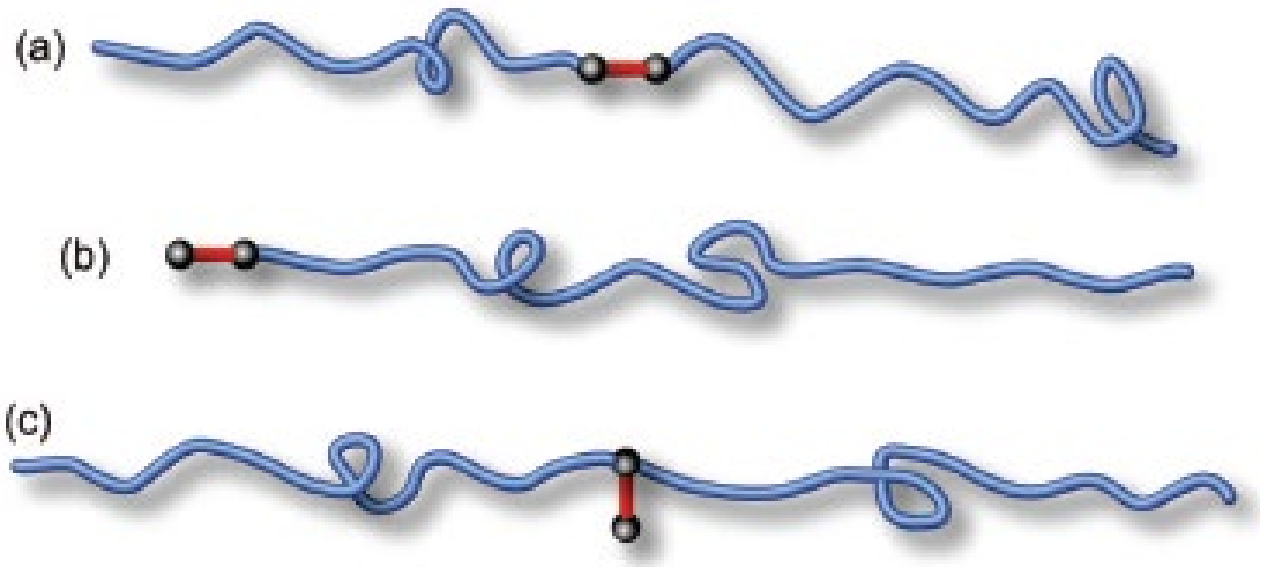


Figure 3. Schematics of a bifunctional mechanophore (a) and control molecules containing a mechanophore linkage at the polymer chain end (b) or in the center of the chain (c). The mechanophore is colored in red for emphasis.

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Bond Specific Activation

Mechanophores ….. possess strategically weakened bonds that undergo useful reactions when force is transferred to the mechanophore from the polymer chain segments

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Mechanophore Design

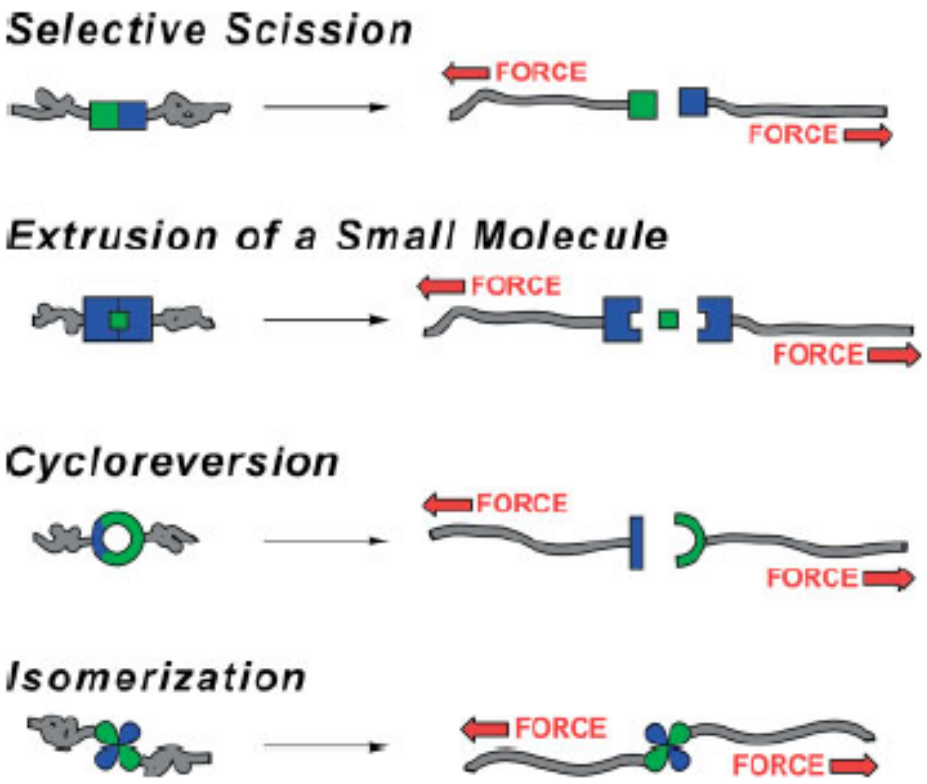


Figure 2. Generalized examples of polymer-embedded mechanophores and their responses to the application of force.

Brantley *et al., Polym Int* **2013**; 62: 2–12

Bond-specific Activation

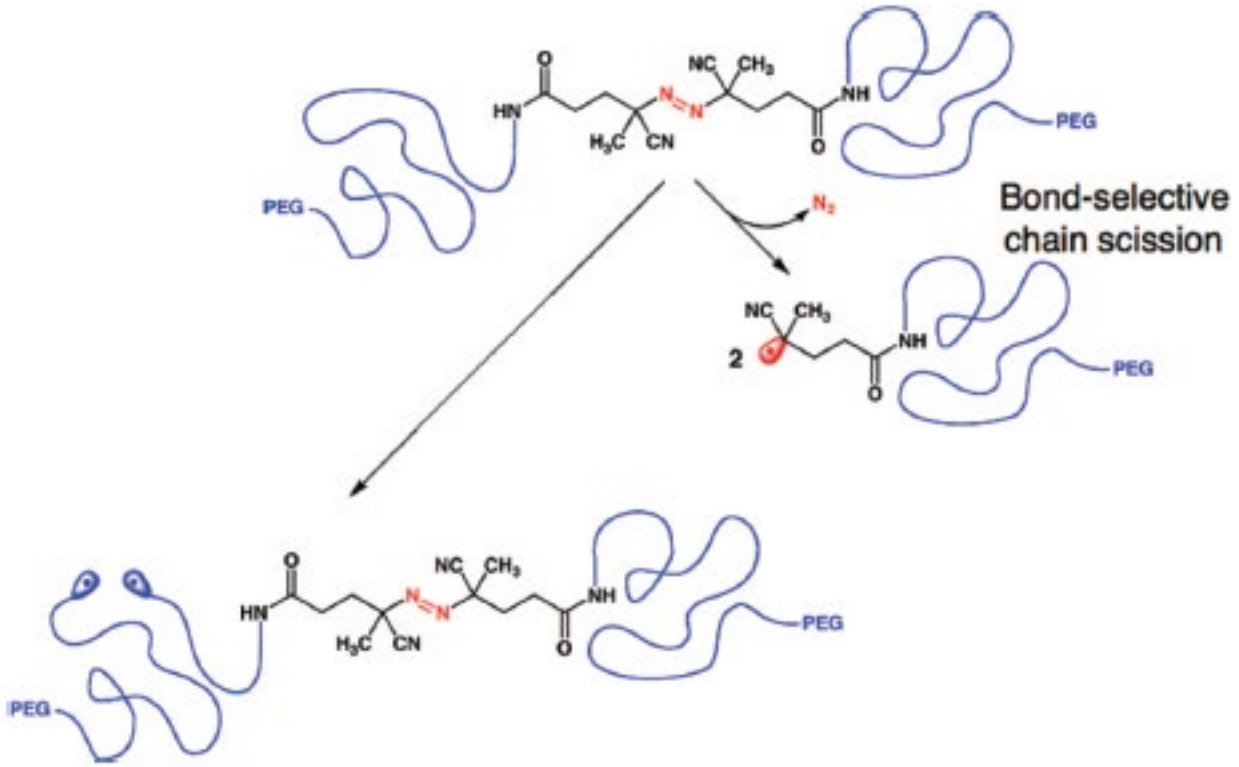


Figure 25. Highly selective bond cleavage for the ultrasound-induced azo-centered PEG chains. For a 30 kDa polymer, selectivity is 1 bond in ca. 1000. Bond-selective chain scission is the predominant pathway.

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Bond-specific Activation

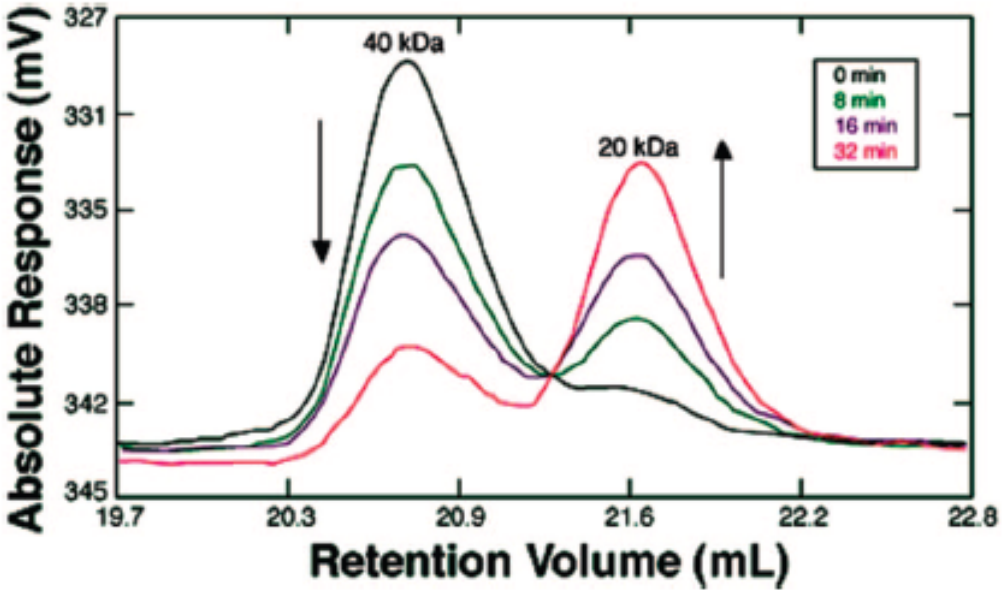


Figure 26. GPC traces showing the chain scission of the 40 kDa PEG azo-linked polymer 1.

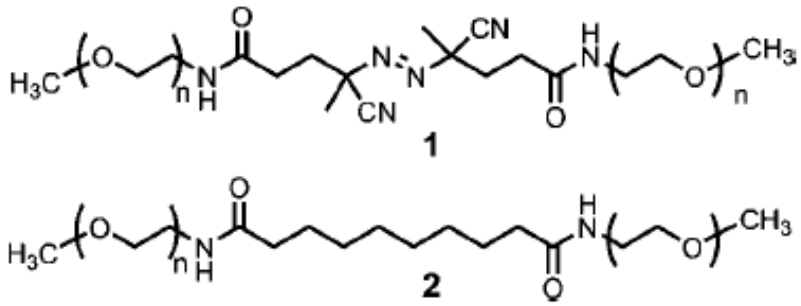


Figure 27. Chemical structures of azo link-functionalized PEG chain (1, top) and sebacic acid (2, bottom) link-functionalized PEG chain.

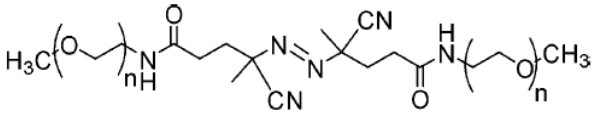
Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Ultrasound-Induced Site-Specific Cleavage of Azo-Functionalized Poly(ethylene glycol)

Kimberly L. Berkowski, Stephanie L. Potisek, Charles R. Hickenboth, and Jeffrey S. Moore*

The Department of Chemistry & The Beckman Institute for Advanced Science and Technology, The University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

Macromolecules **2005,** *38,* 8975−8978



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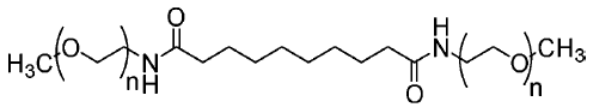


2

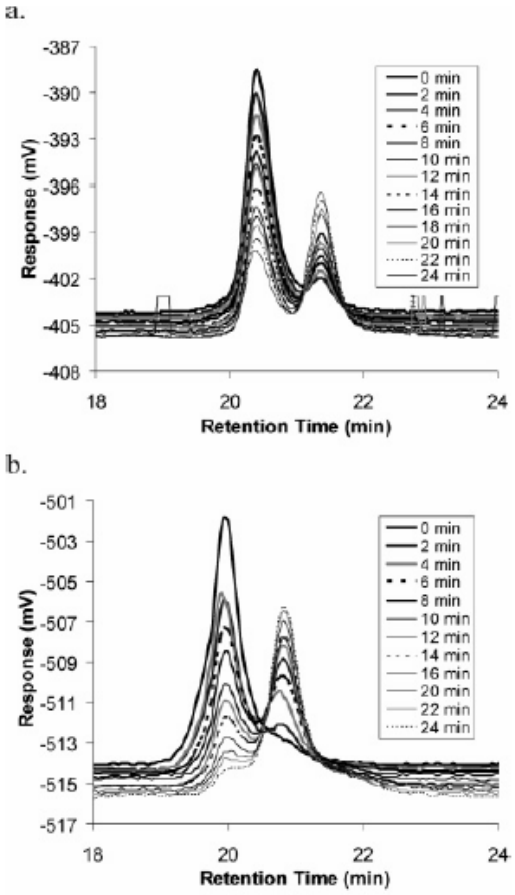
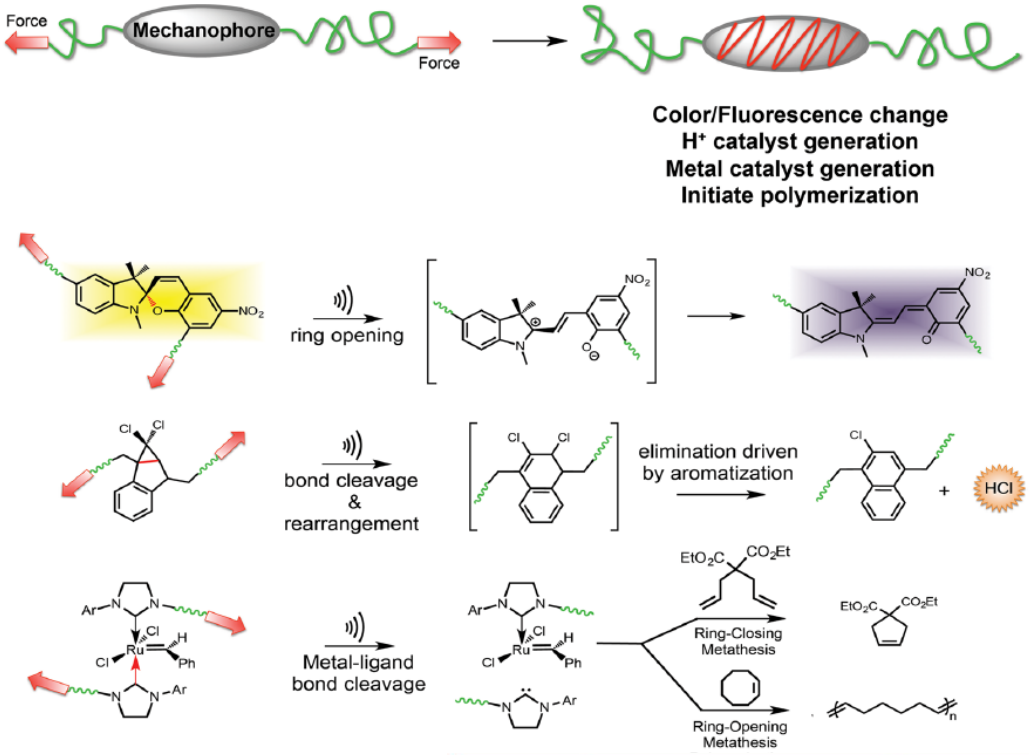
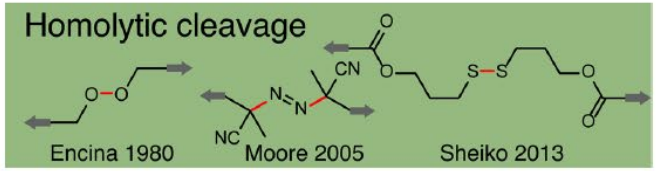
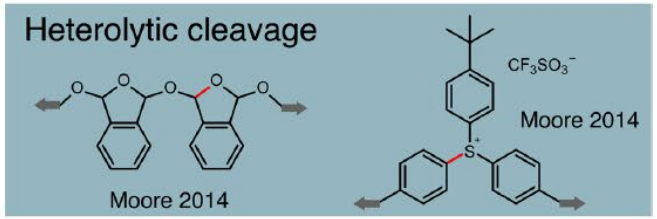


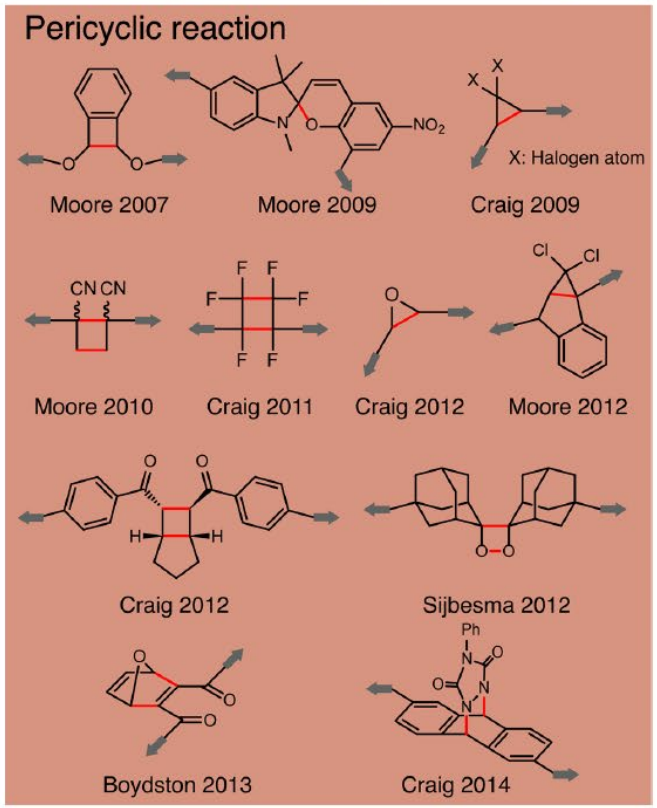
Figure 1. GPC traces depicting the effect of ultrasound on polymer **1** (40 and 60 kDa) and **2** (40 kDa). A 0.75 mg/mL solution of either polymer **1** or control **2** in acetonitrile was subjected to ultrasound, at 20 kHz, 8.7 W/cm^2, and 6−9 °C under argon. (a) Absolute peak areas of 40 kDa polymer **1** starting material and the 20 kDa cleaved fragments at timed intervals throughout sonication. The small 20 kDa peak at $t = 0$ is due to uncoupled 20 kDa mPEG-NH_2 starting material, from the synthesis of **1**, that could not be separated. (b) Absolute peak areas of 60 kDa polymer **1** starting material and the 30 kDa cleaved fragments at timed intervals throughout sonication. (c) Absolute peak areas of 40 kDa control **2** starting material at timed intervals throughout sonication.

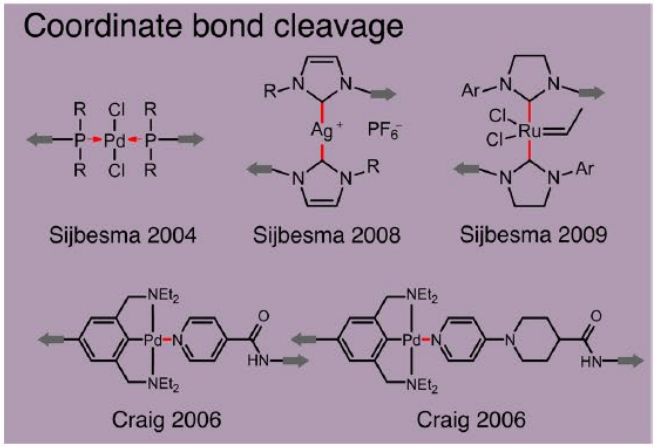
Other Mechanophores











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Acc. Chem. Res. 2015, 48, 2181−2190

Soft Mechanochemistry

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Soft-Mechanochemistry: Mechanochemistry Inspired by Nature

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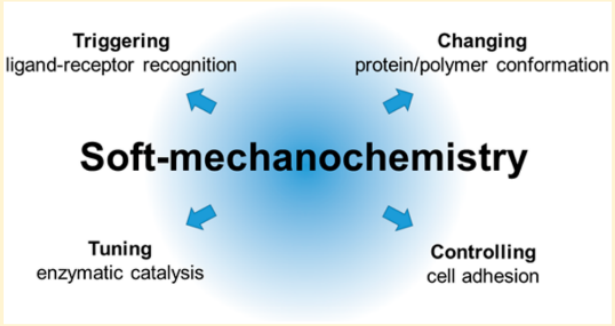
Supporting Information

ABSTRACT: Cells and bacteria use mechanotransduction processes to transform a mechanical force into a chemical/biochemical response. The area of chemistry where chemical reactions are induced by mechanical forces is called mechanochemistry. Over the last few years, chemists developed force-induced reactions affecting covalent bonds in molecules under tension which requires high energy input and/or high intensity forces. In contrast, in nature, mechanotransduction processes take place with forces of much weaker intensity and much less demanding energy. They are mainly based on protein conformational changes or changes in supramacromolecular architectures. Mechanochemistry based on such low-energy-demanding processes and which does not affect chemical bonds can be called soft-mechanochemistry.

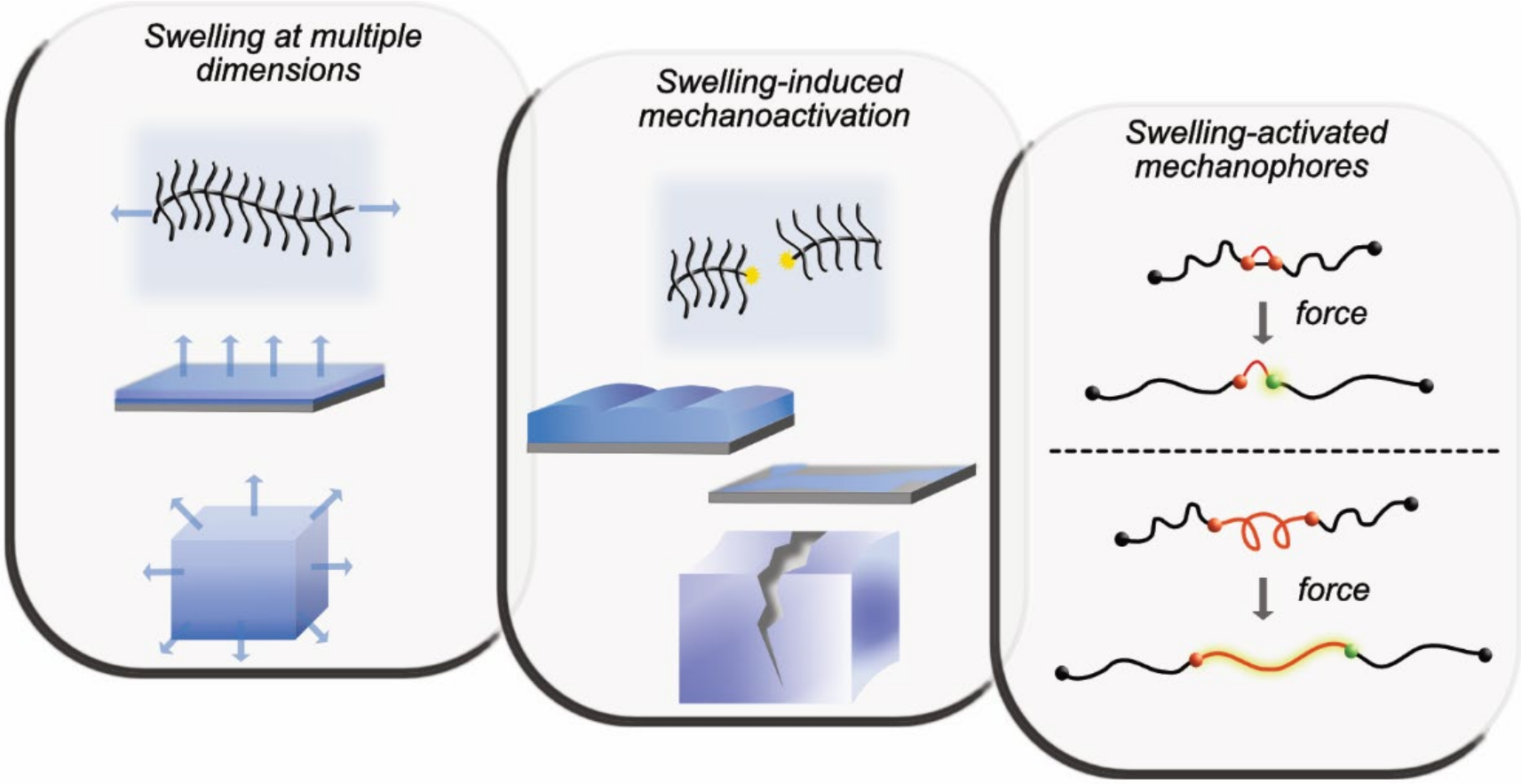


In this feature article, we first discuss some examples of soft-mechanochemistry processes encountered in nature, in particular, cryptic sites, allowing us to define more precisely the concepts underlying soft-mechanochemistry. A series of examples, developed over the past few years, of chemomechanoresponsive systems based on soft-mechanochemistry principles are given. We describe, in particular, cryptic site surfaces, enzymatically active films whose activity can be modulated by stretching and films where stretching induces changes in their fluorescence properties. Finally, we give our view of the future of soft-mechanochemistry.

P. Lavalle, F. Boulmedais, P. Schaaf, L. Jierry, *Langmuir* **2016**, *32*, 7265

Swelling-Activated, Soft Mechanochemistry

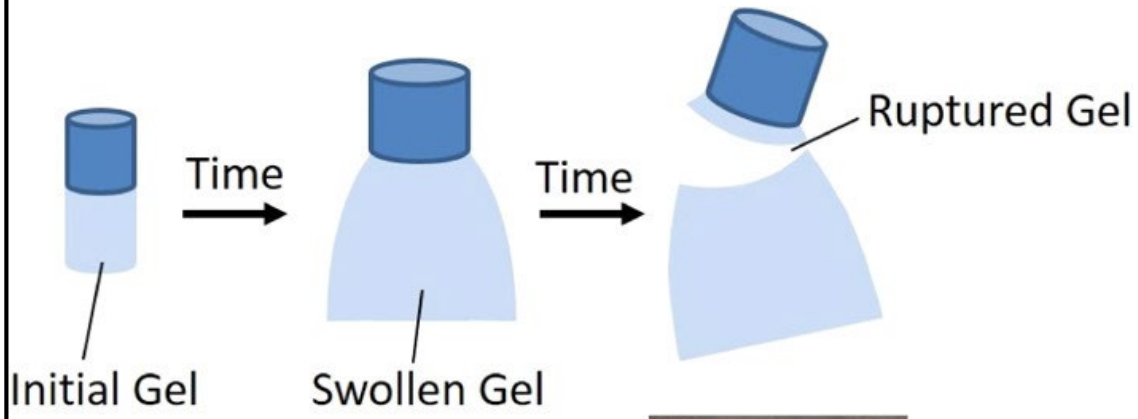
Solvent Swelling can Accelerate Bond Cleavage Events

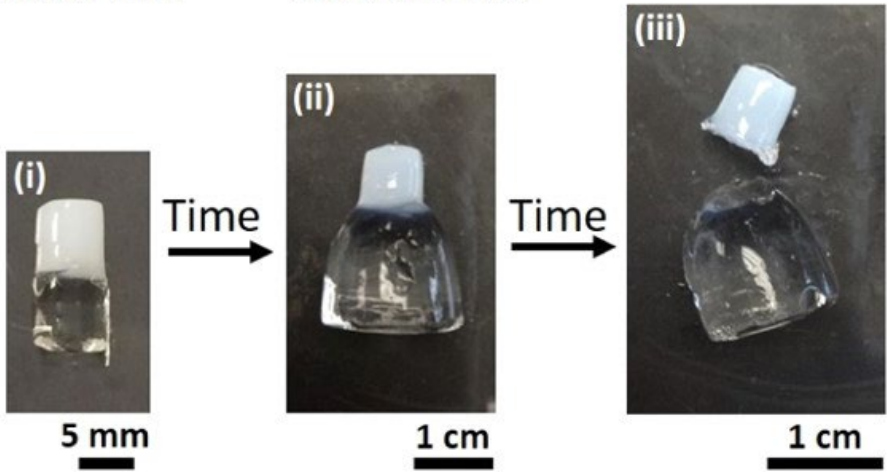


F. K. Metze, S. Sant, Z. Meng, H.-A. Klok, K. Kaur, *Langmuir* **2023**, *39*, 3546-3557

Swelling-Induced Failure of Soft Matter

Self-rupturing *N*,*N*-ethylenebis(acrylamide) crosslinked poly(acrylic acid) hydrogels



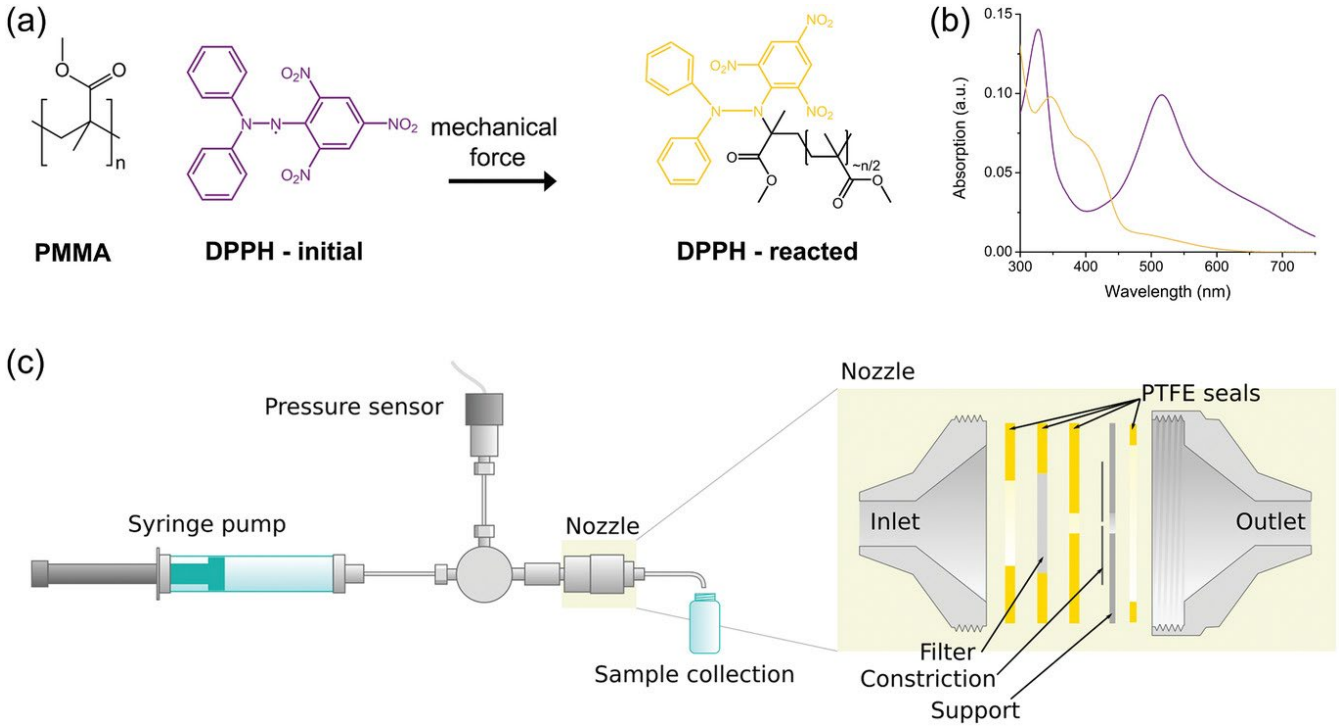


U. K. de Silva, Y. Lapitsky, *ACS Appl. Mater. Interfaces* **2016**, *8*, 29015

What is the molecular origin of this macroscopic, catastrophic failure of soft materials ?

How can this be measured?

Flow Set Ups



Willis-Fox et al. Adv. Funct. Mater. 2020, 30, 2002372

Rheometers

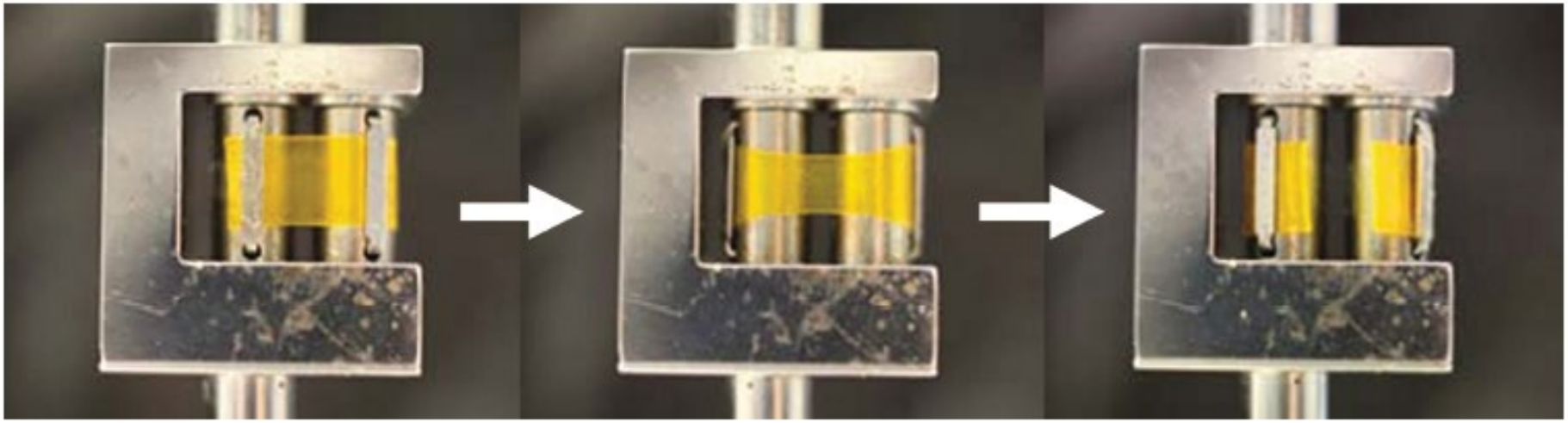


Fig. 6 Images showing the elongation of a polymer film by a rheometer with an extension fixture. Reprinted with permission from Macmillan Publishers Ltd: ref. 43, 2012.

Wiggins *et al., Chem.Soc.Rev.,* **2013**, 42, 7130-7147

Tensile Testing Instruments

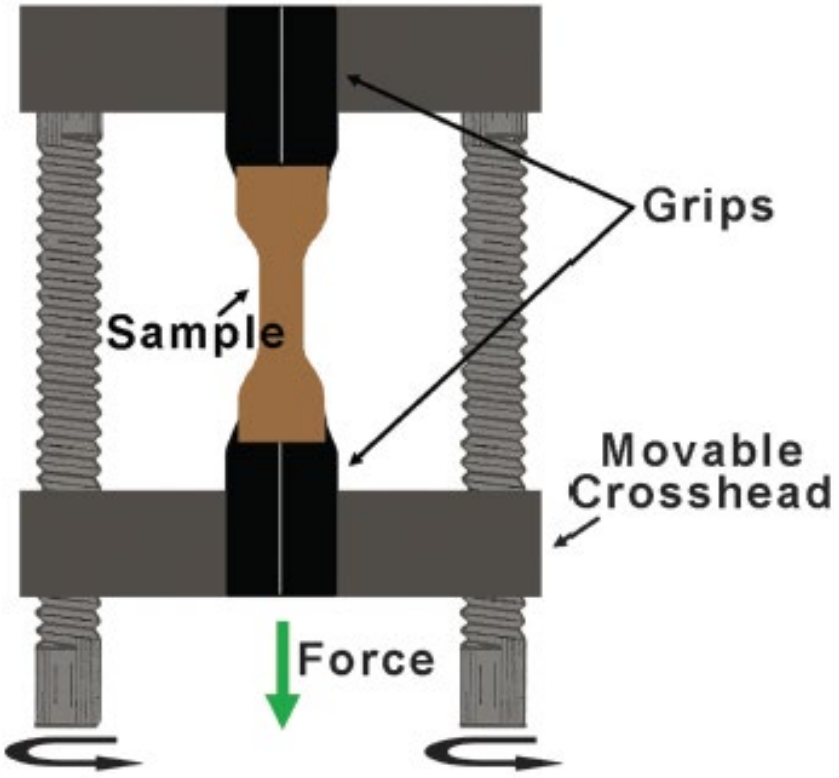


Fig. 8 Schematic drawing of the components of a typical tensile testing instrument.

Wiggins *et al., Chem.Soc.Rev.*, **2013**, 42, 7130-7147

Mechanically-activated luminescence

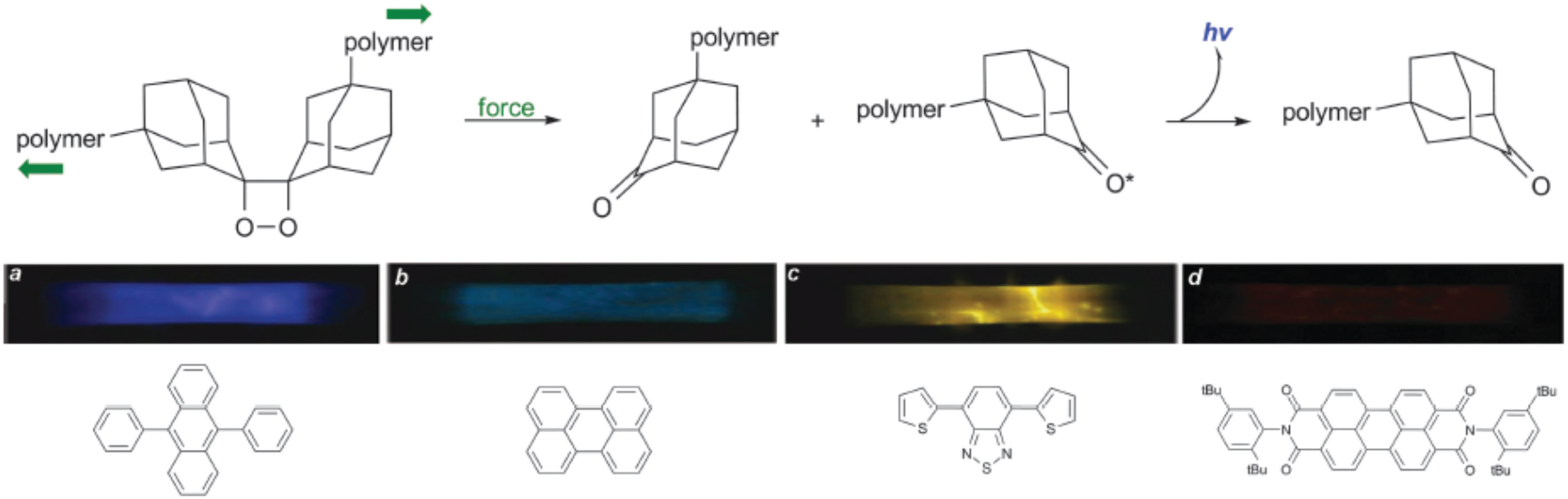
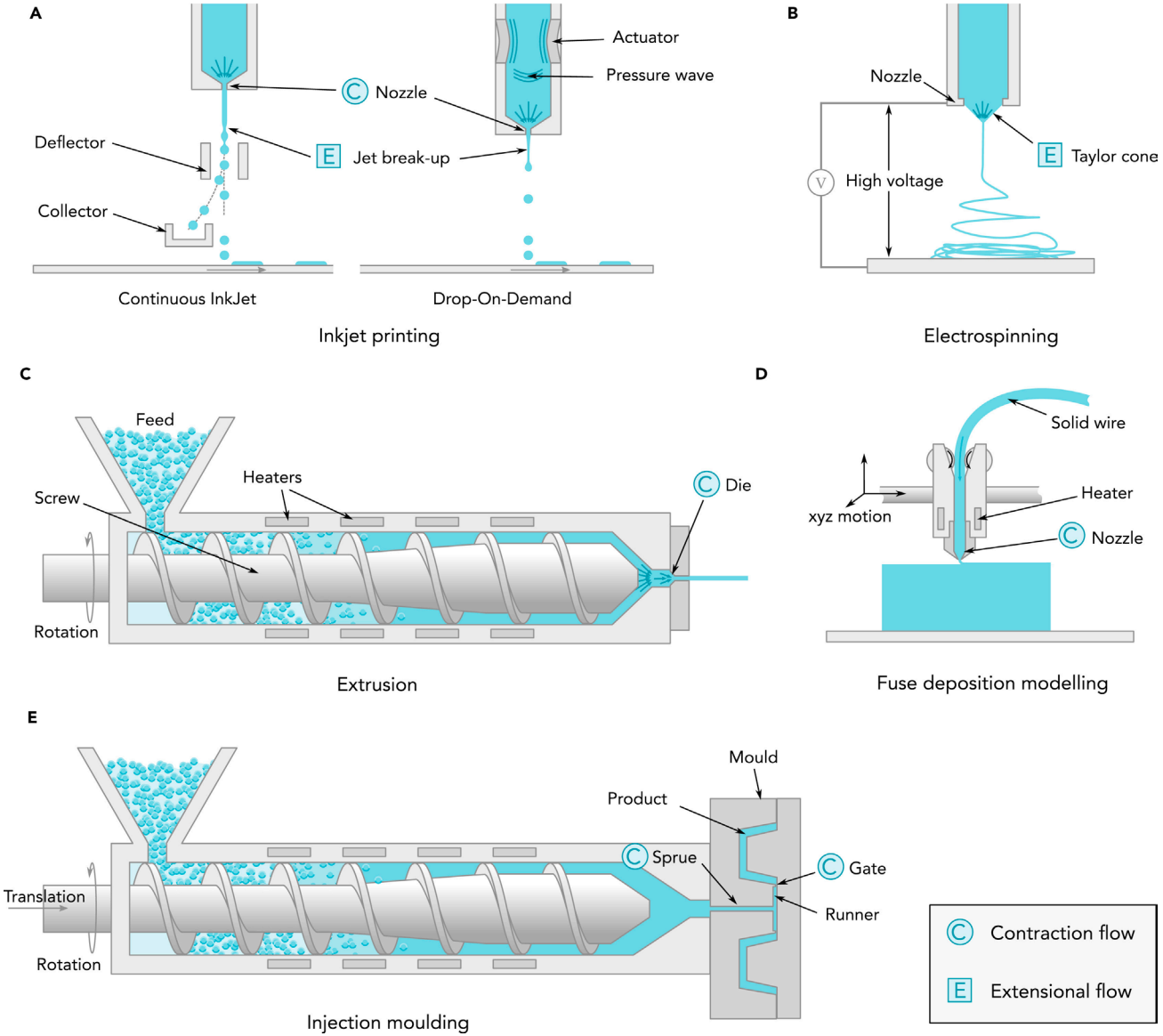


Fig. 7 (top) Mechanical cycloreversion of a polymer embedded 1,2-dioxetane unit resulted in the formation of an electronically excited keto-intermediate that relaxed via blue chemiluminescence. The green arrows indicate the direction of the applied force. (bottom) Optical images and structures of various acceptor molecules blended into poly(methyl acrylate) materials containing 1,2-dioxetane-based crosslinkers: (a) 9,10-diphenylanthracene, (b) perylene, (c) 4,7-di(thiophen- 2-yl)-benzo[c][1,2,5] thiadiazole and (d) N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene dicarboximide. polymer = poly(methyl acrylate). Images reprinted with permission from Macmillan Publishers Ltd: ref. 43, 2012.

Wiggins *et al., Chem.Soc.Rev.,* **2013**, 42, 7130-7147

Applications

Processing & Mechanochemistry



Willis-Fox, et al. Chem 2018, 4, 2499–2537

Self-healing Materials

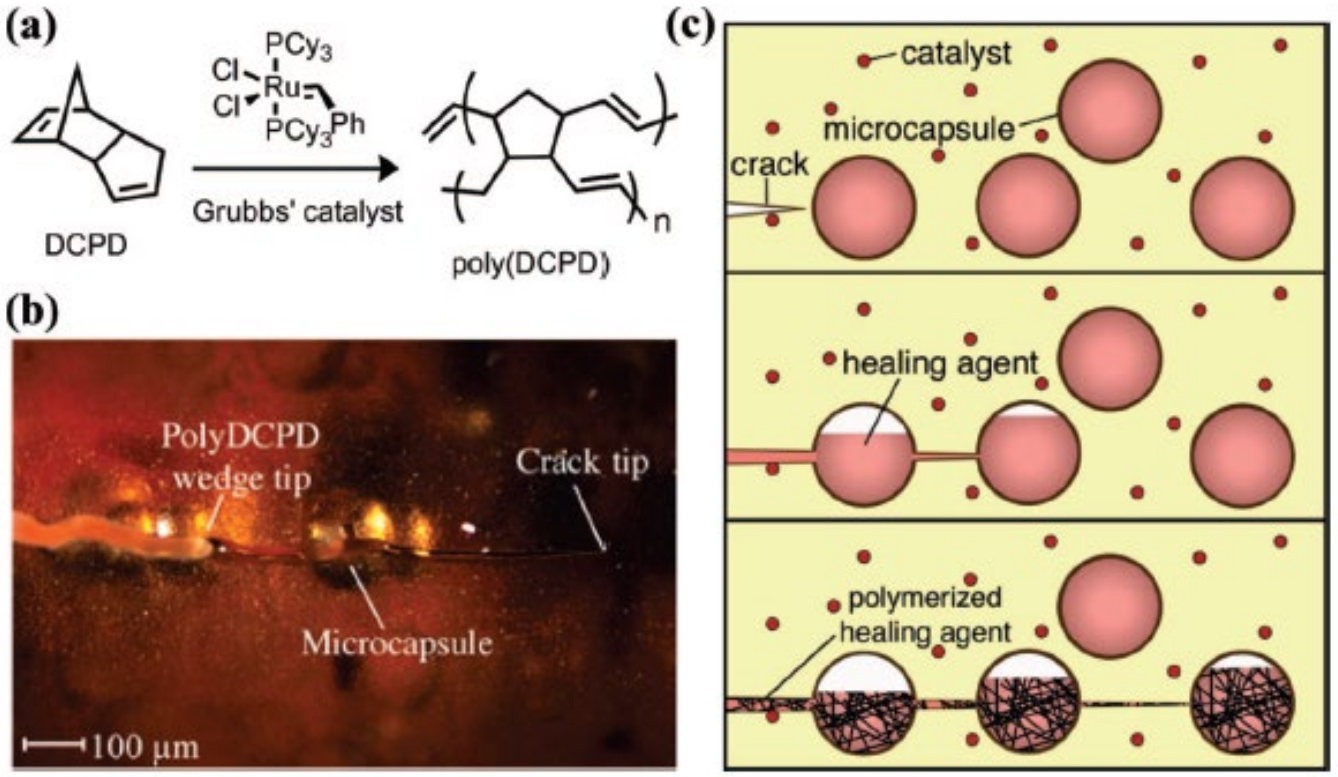


Figure 49. (a) Reaction scheme of the monomer DCPD undergoing ring-opening metathesis polymerization to form poly(DCPD). (b) Optical micrograph of an *in situ* fatigue specimen showing poly(DCPD) formed in the crack plane behind the crack tip. Reprinted with permission from ref 362. Copyright 2005 Elsevier. (c) The autonomic self-healing system showing crack initiation, rupture of microcapsules, and release of healing agent, and the resulting polymer formed in the crack plane.

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Other Microencapsulated Self-Healing Chemistries

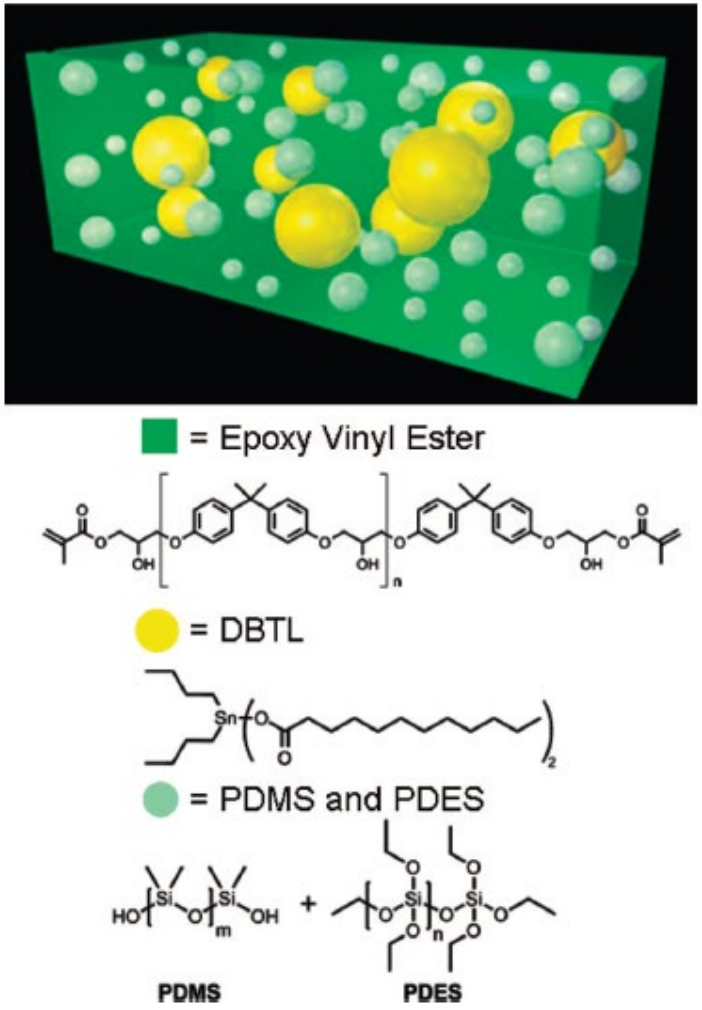


Figure 52. Schematic of the phase-separated PDMS self-healing system and chemical structures of each component. Reproduced with permission from ref 386. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

Caruso et al. *Chem. Rev.* **2009,** *109,* 5755–5798

Mechanochemical activation of latent catalysts (“mechanocatalysis”)

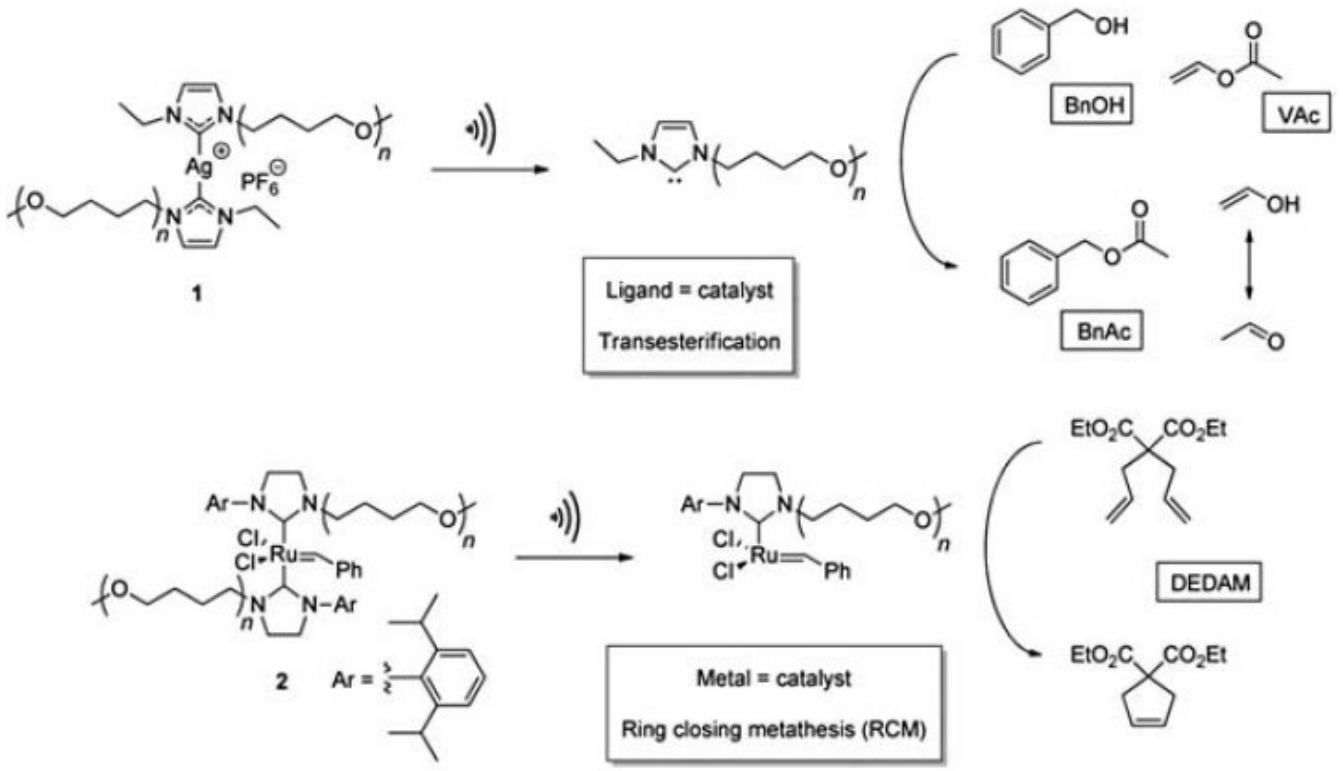
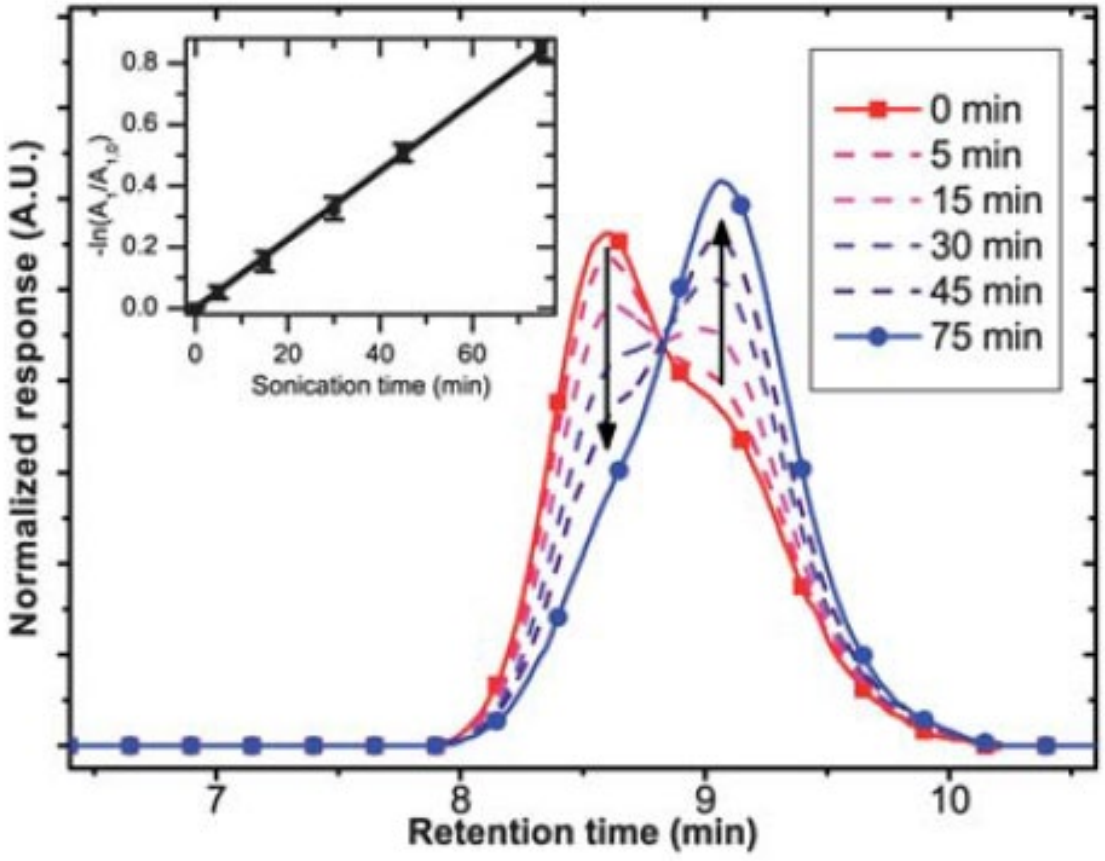


Fig. 4 Overview of latent mechanocatalyst complexes and catalytic reactions.

Groote *et al., Polym. Chem.,* **2013**, **4**, 4846–4859

Scission of a mechanocatalyst can be followed by GPC



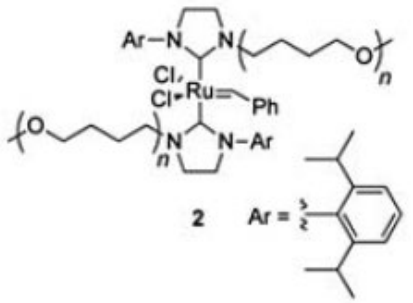
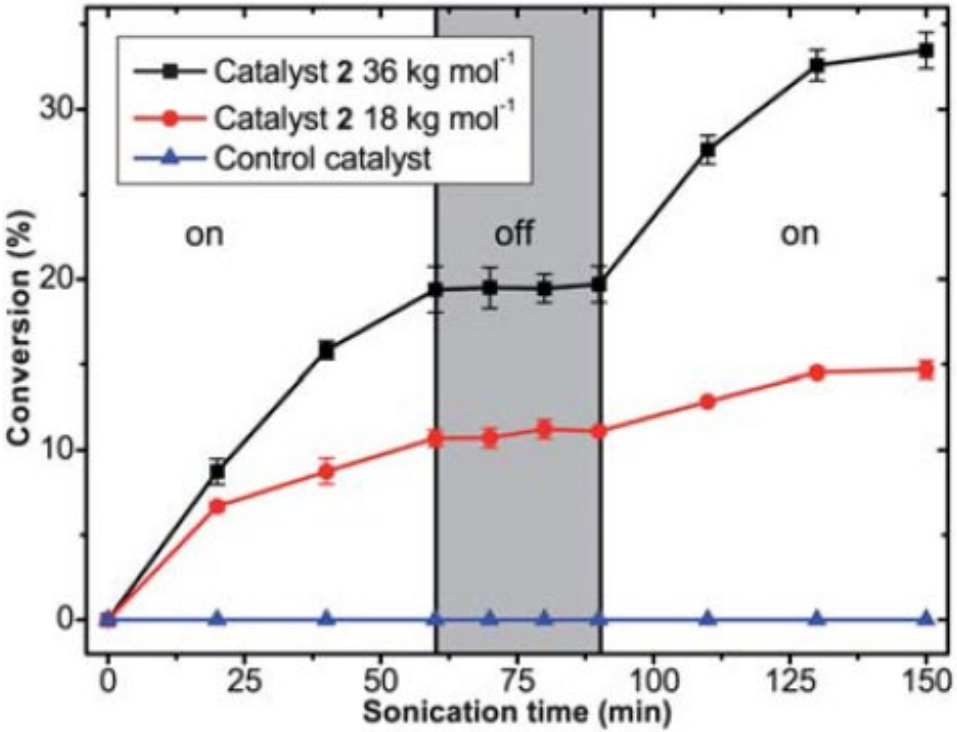


Fig. 6 GPC traces of catalyst **2** before and during sonication. Inset shows the first order kinetics plot of the area of the peak in GPC ascribed to **2**.

Groote *et al., Polym. Chem.,* **2013**, **4**, 4846–4859

Catalysis shows expected molecular weight dependence



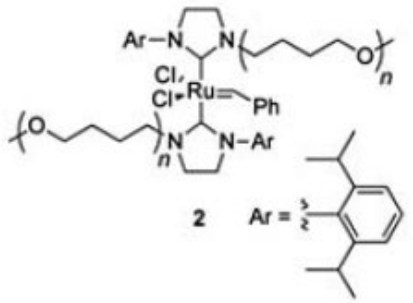


Fig. 7 Time–conversion plot for the sonication of DEDAM in the presence of catalyst **2** (18 or 36 kg mol^{-1}) or a low molecular weight control catalyst. Sonication: 60 min on, 30 min off, 60 min on.

Groote *et al., Polym. Chem.,* **2013**, **4**, 4846–4859