Mathematical modelling of biodegradable polymers

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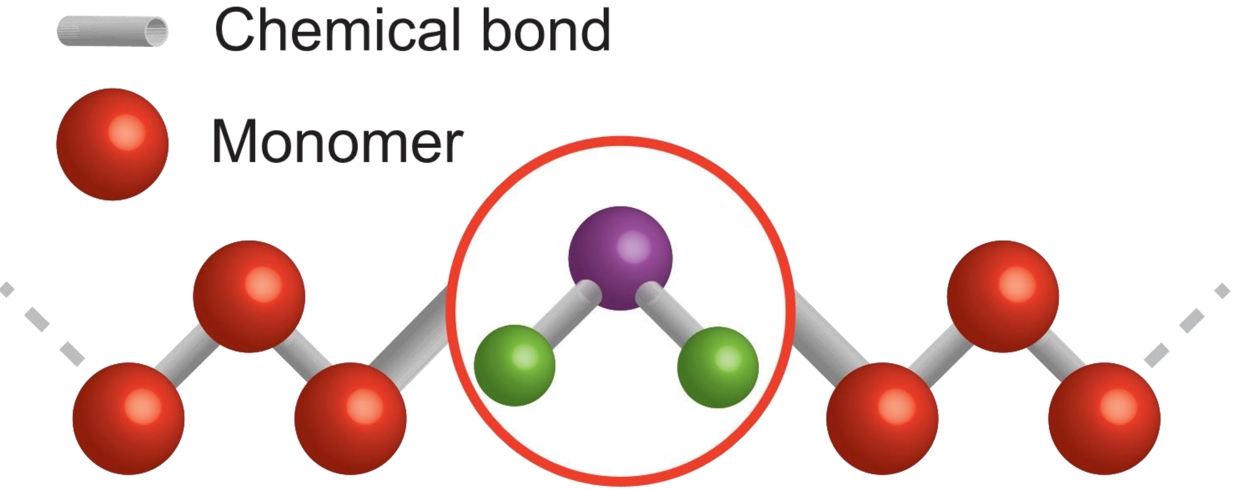
Biodegradable polymers



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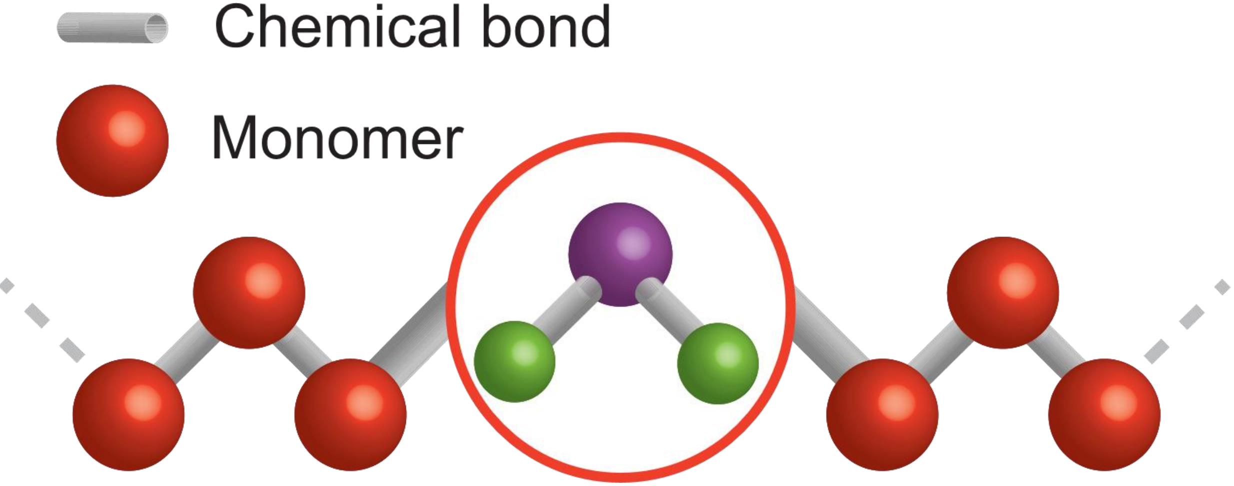
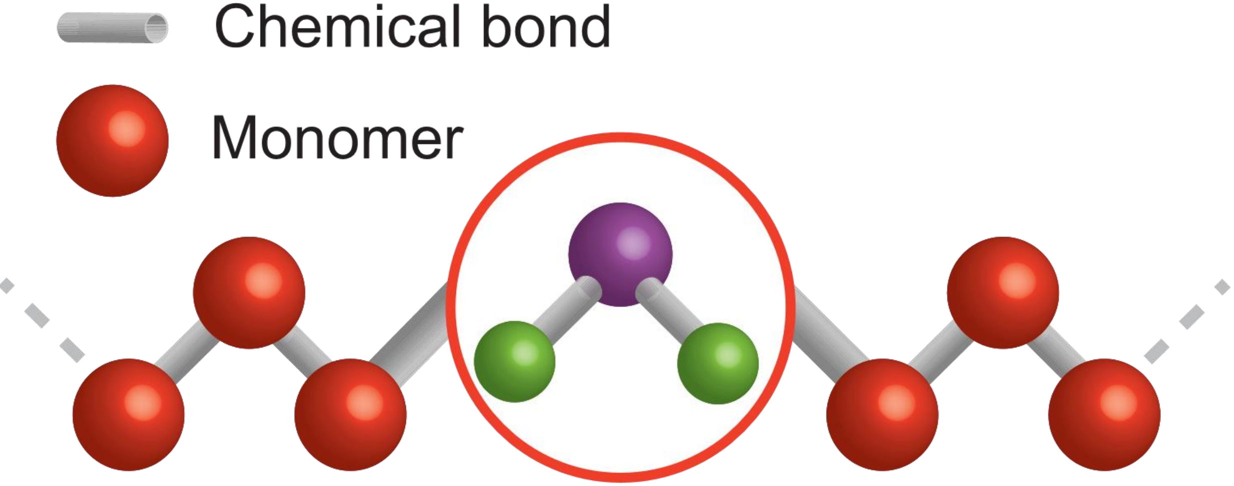


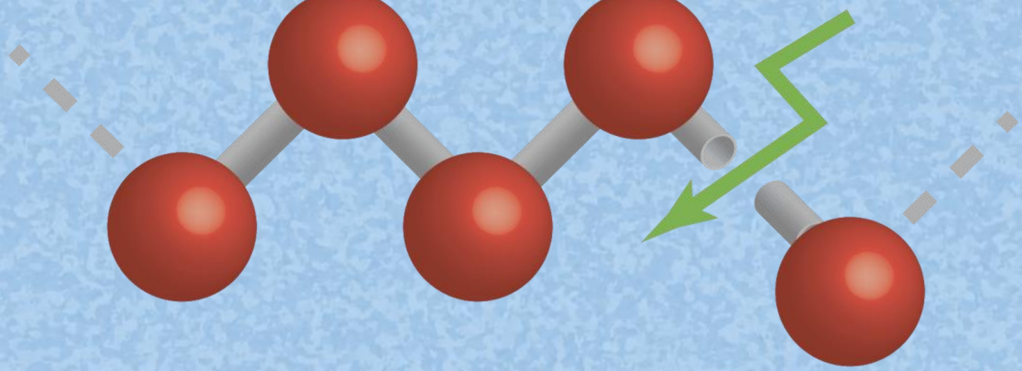
Amorphous

Biodegradable polymers



Amorphous

Hydrolysis – scission of bonds



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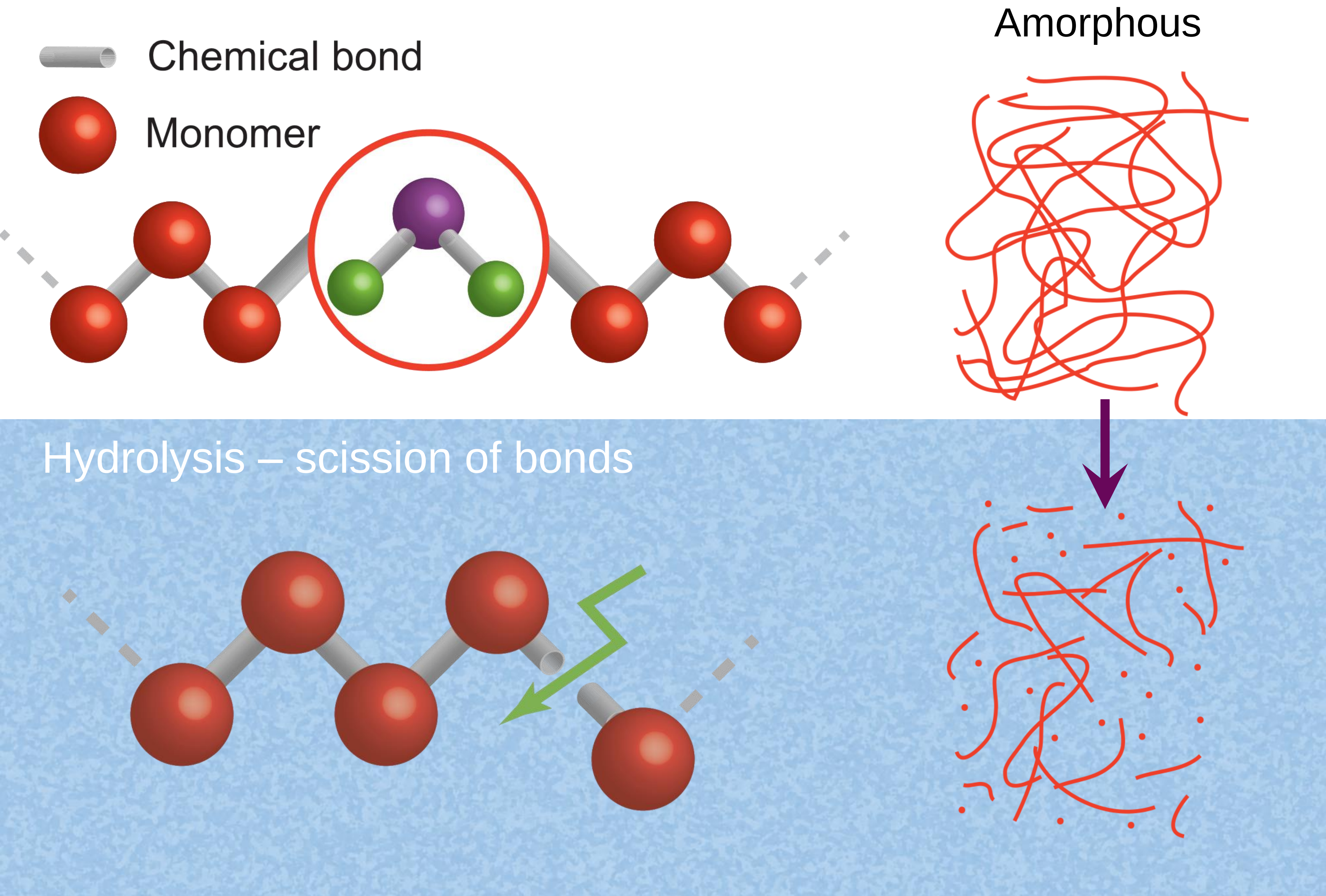
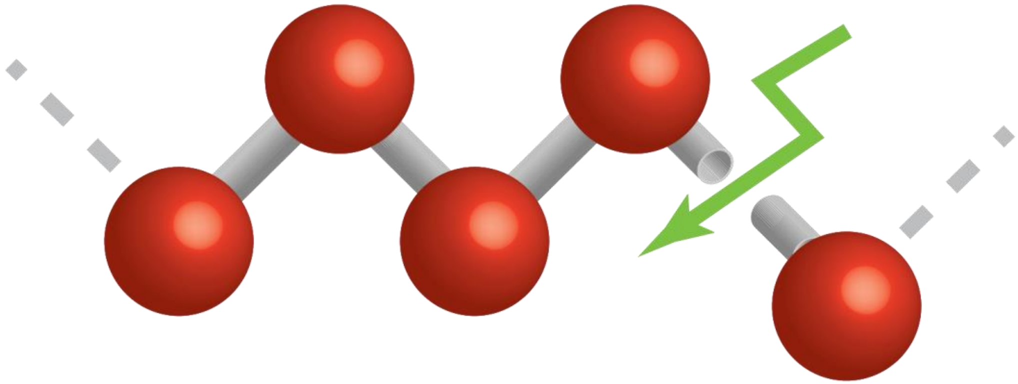


Hydrolysis



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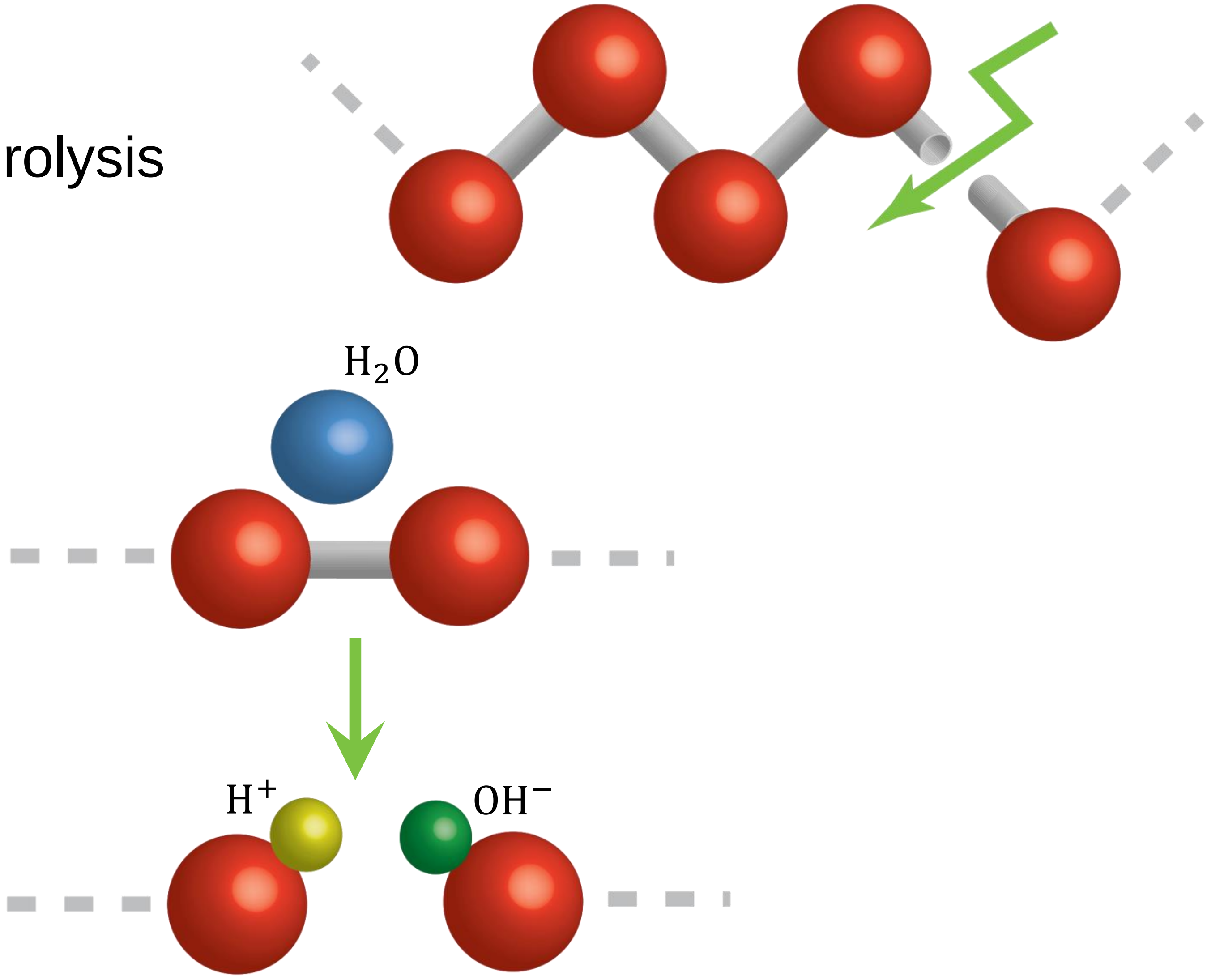

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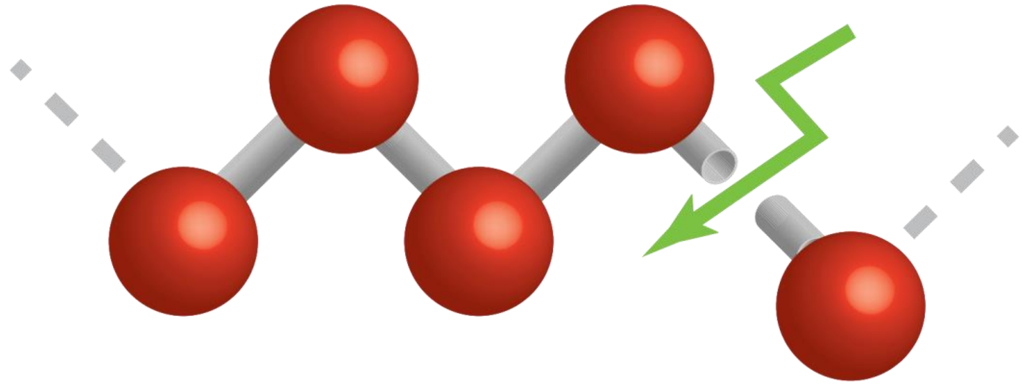
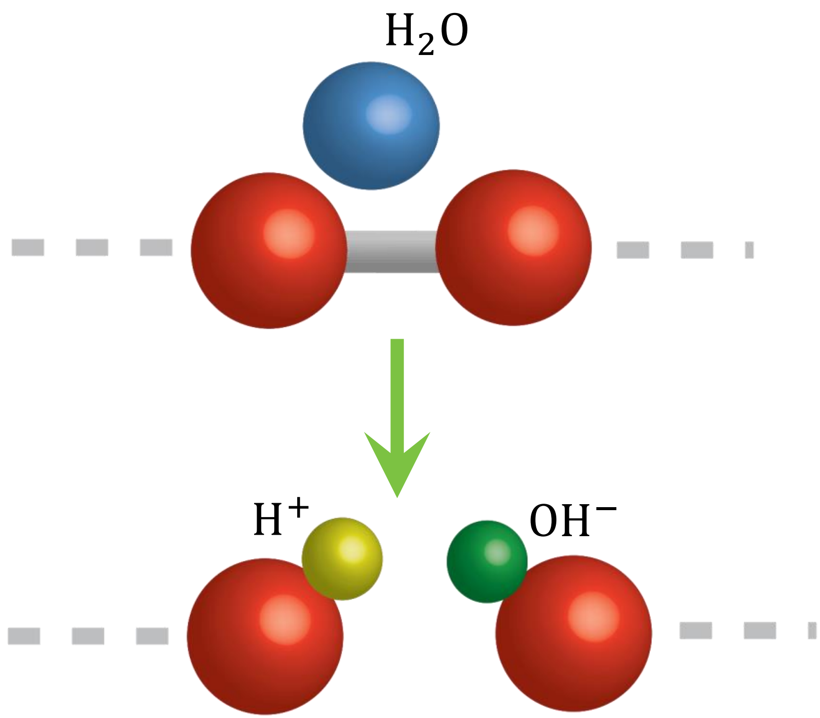
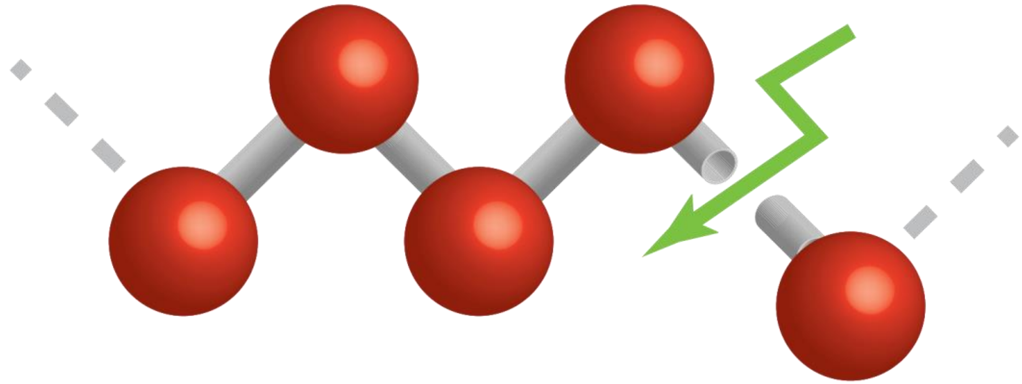
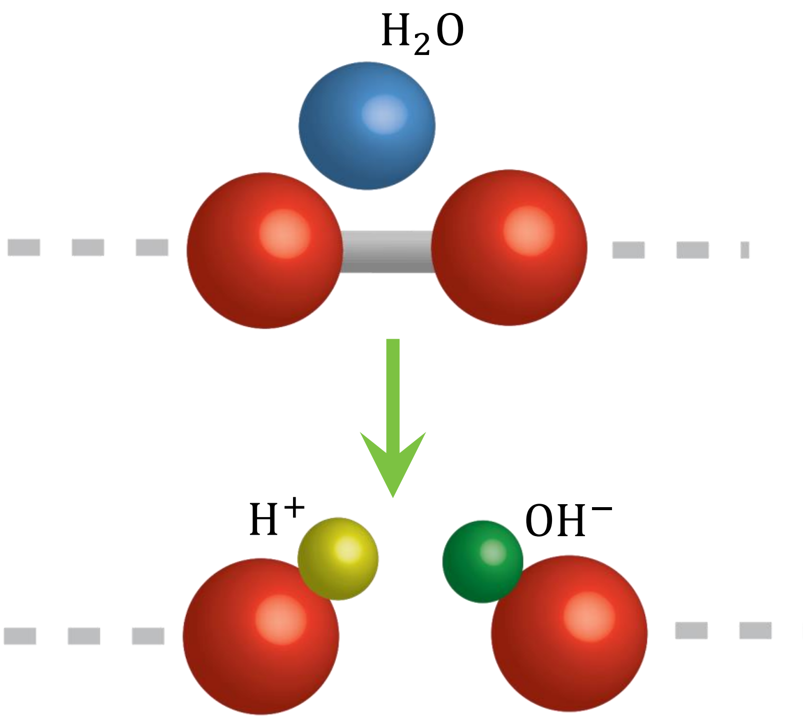


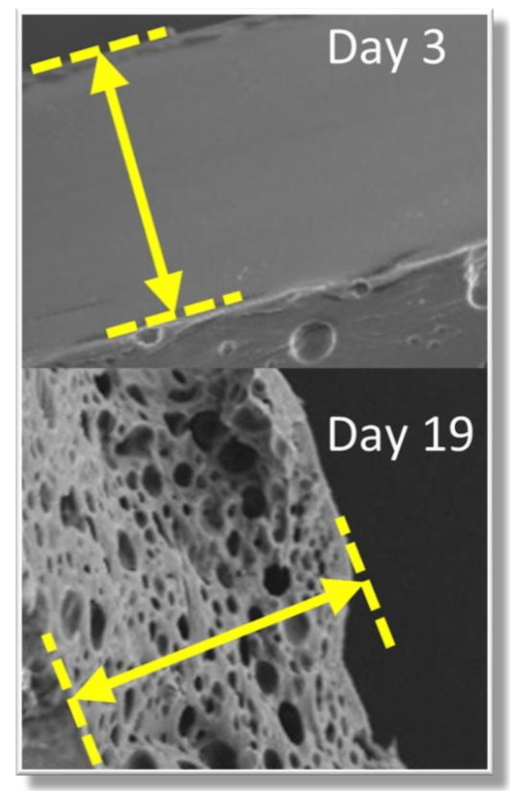


Autocatalysis – hydrolysis accelerated by acidic degradation products

Hydrolysis



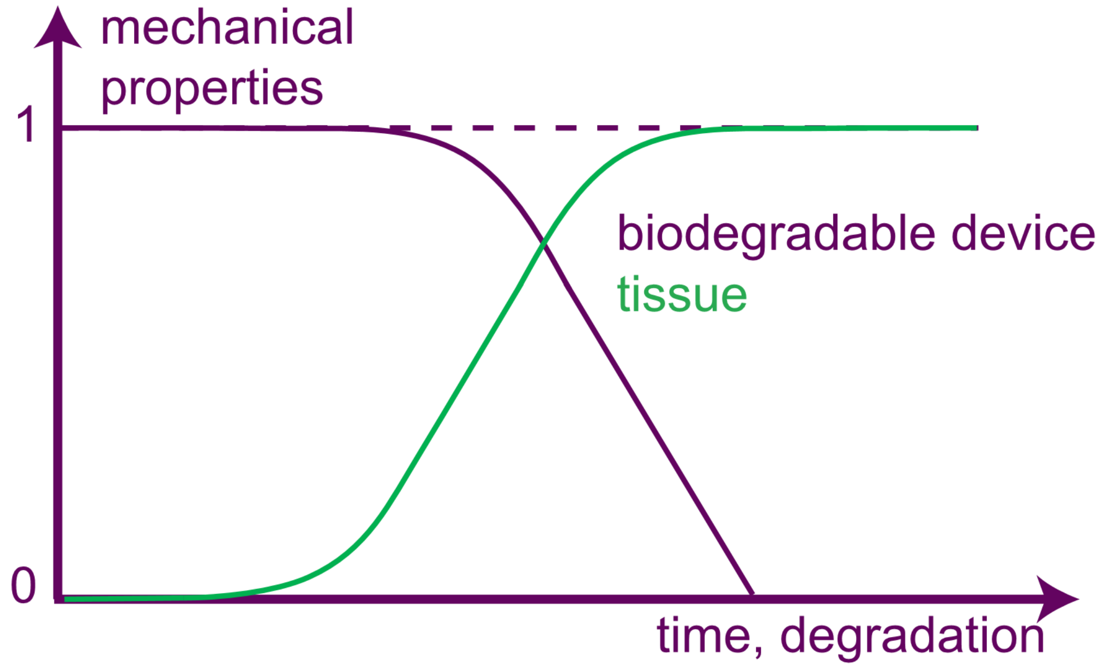




Autocatalysis – hydrolysis accelerated by acidic degradation products

Shirazi et al., Acta Biomaterialia, **10**:4695-4703, 2014.

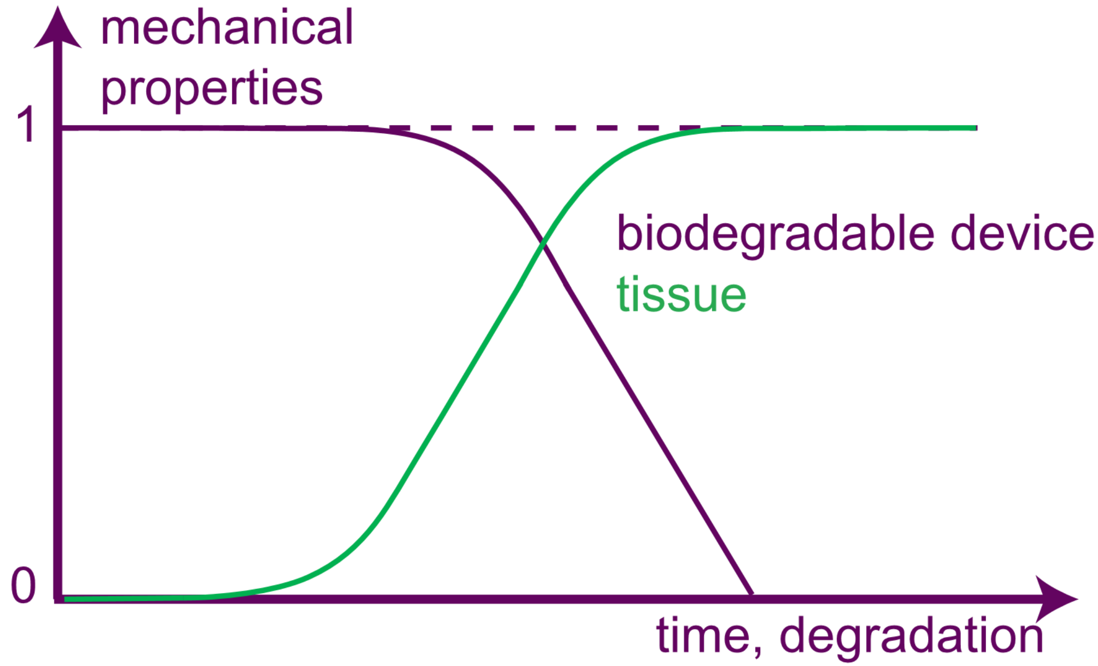
How do polymer properties evolve as degradation occurs?



How do polymer properties evolve as degradation occurs?

Sufficient mechanical integrity

Suitable degradation rate



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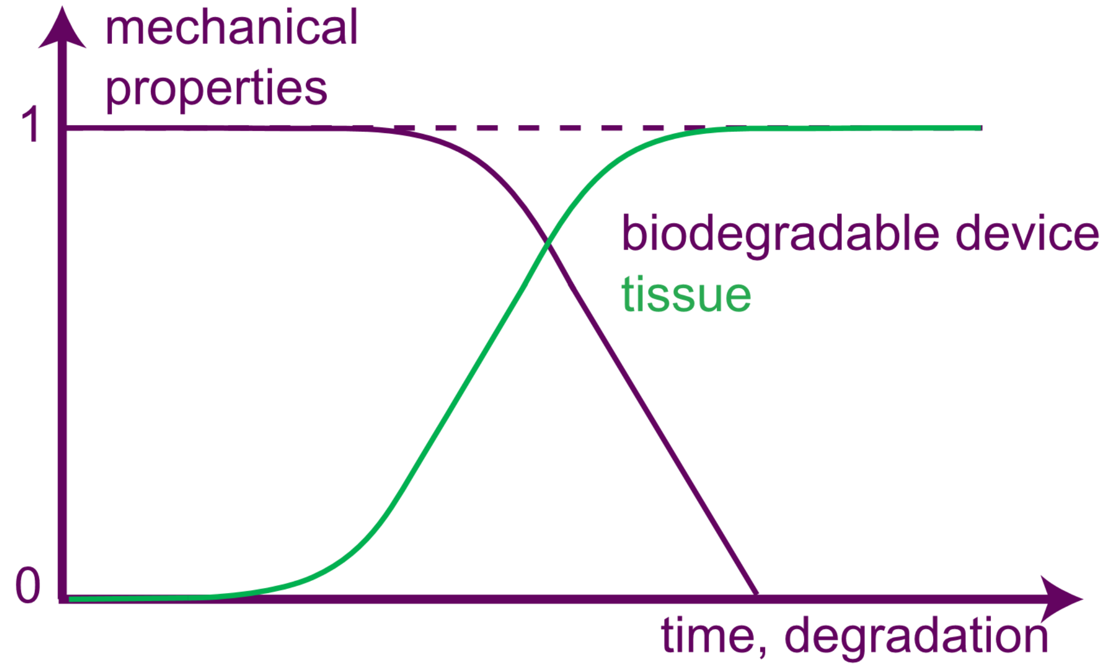

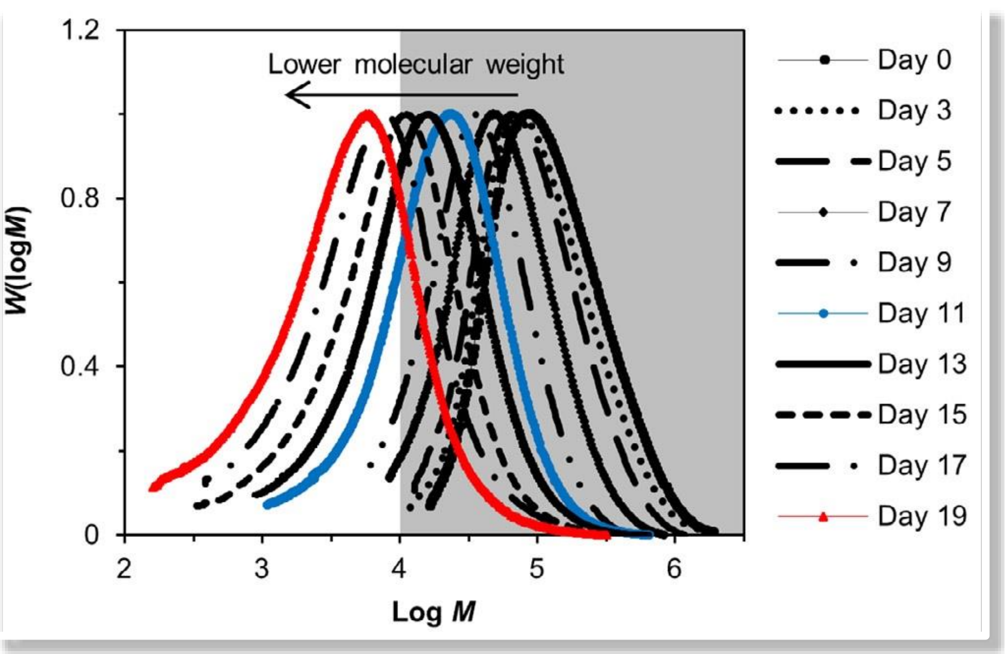

Number average molecular weight:

$$M_n = \frac{\sum M_i N_i}{\sum N_i}$$

N_i - number of chains of weight M_i

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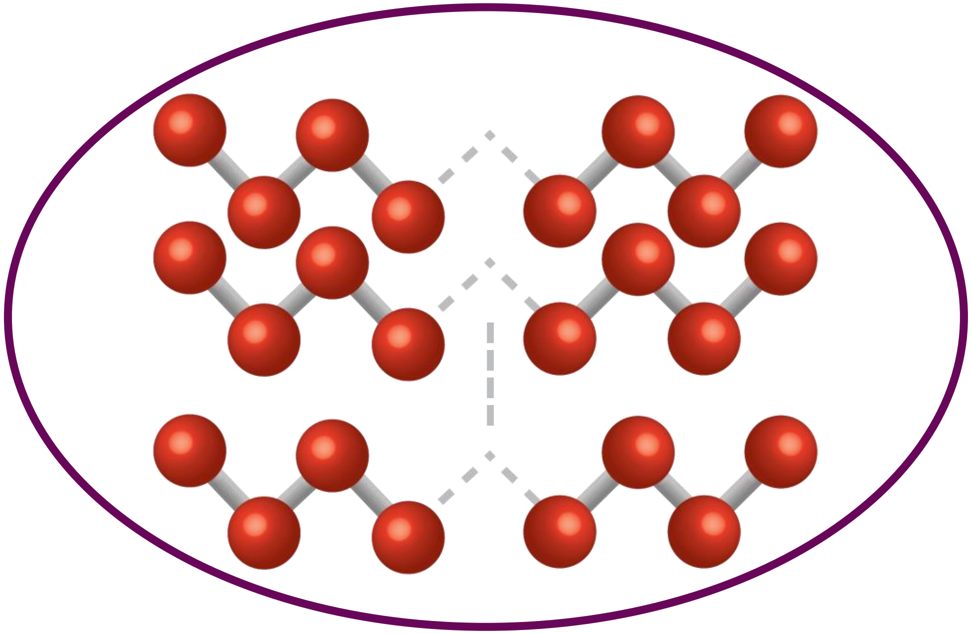
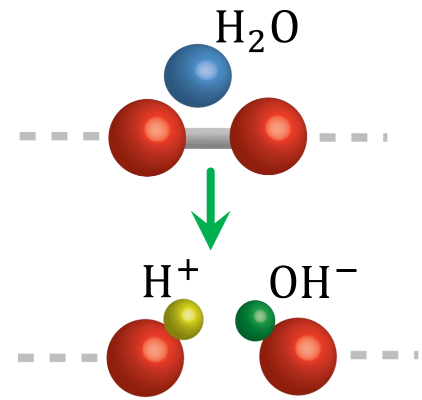
Kinetic model (closed system)





$$bonds = bonds - 1$$

$$acid\ ends = acid\ ends + 1$$

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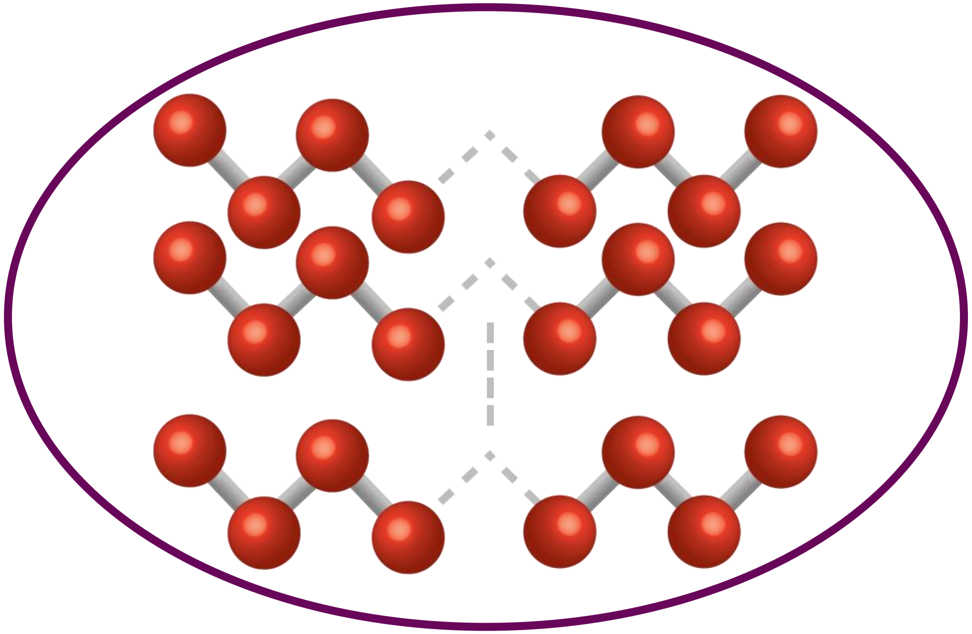

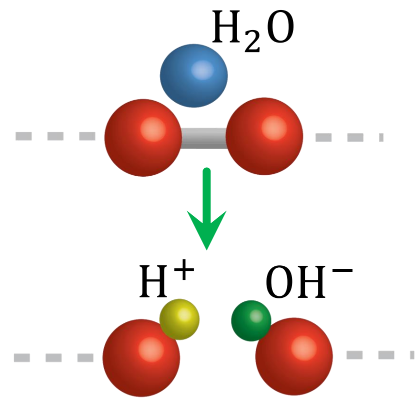

$$bonds = bonds - 1$$

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Change in ester bond concentration

$$\frac{dC_e}{dt} = -(k_h C_e + k_a C_e C_a^{0.5})$$

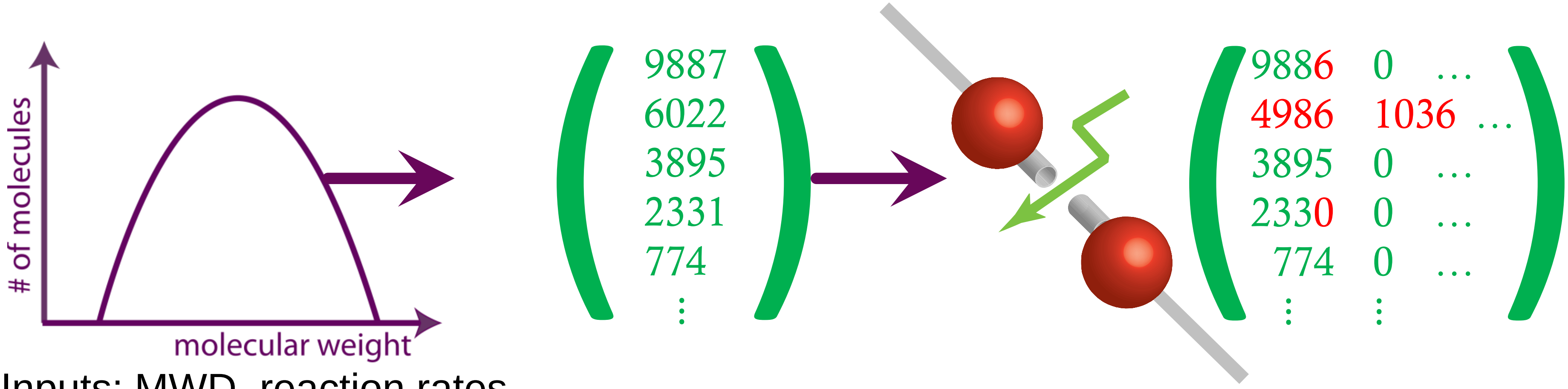
Non-catalytic degradation mechanism

Autocatalytic degradation mechanism

Change in acid chain end concentration

$$\frac{dC_a}{dt} = k_h C_e + k_a C_e C_a^{0.5}$$

Kinetic scission model



Inputs: MWD, reaction rates

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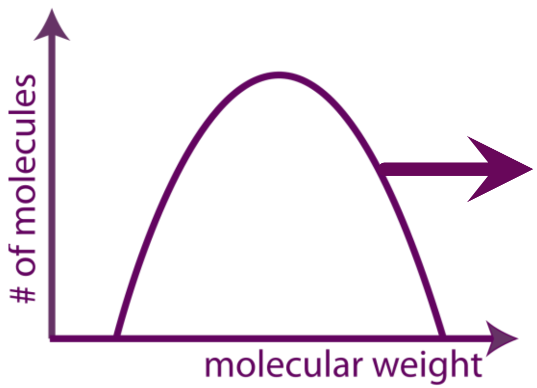
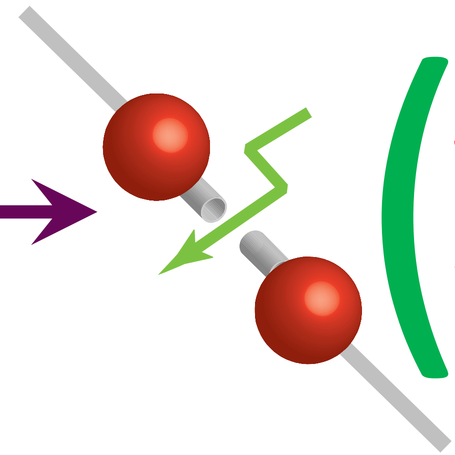


$$\begin{pmatrix} 9887 \\ 6022 \\ 3895 \\ 2331 \\ 774 \\ \vdots \end{pmatrix} \rightarrow$$



$$\begin{pmatrix} 9886 & 0 & \dots \\ 4986 & 1036 & \dots \\ 3895 & 0 & \dots \\ 2330 & 0 & \dots \\ 774 & 0 & \dots \\ \vdots & \vdots & \end{pmatrix}$$

Inputs: MWD, reaction rates

Scissions per time-step:

$$EndScissions = k_{he}C_e + k_{ae}C_eC_a^{0.5}, \qquad RandomScissions = k_{hr}C_e + k_{ar}C_eC_a^{0.5}$$

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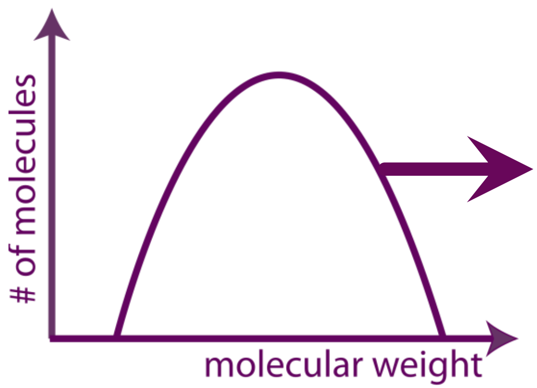

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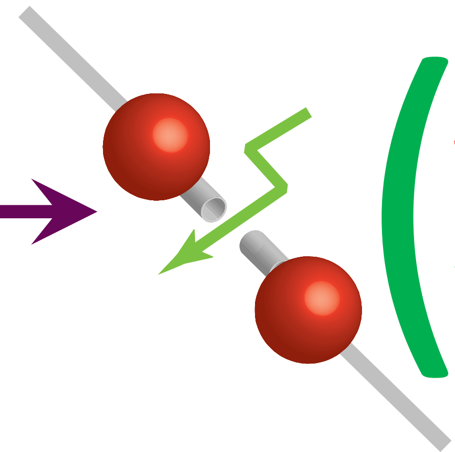

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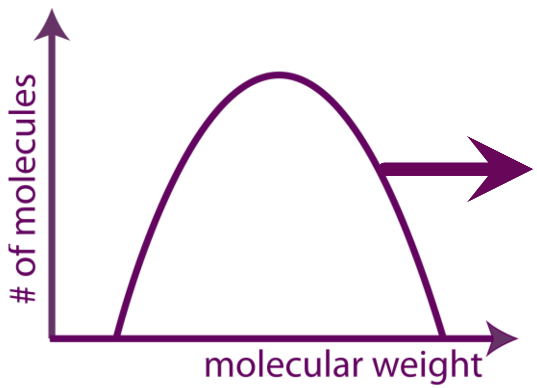

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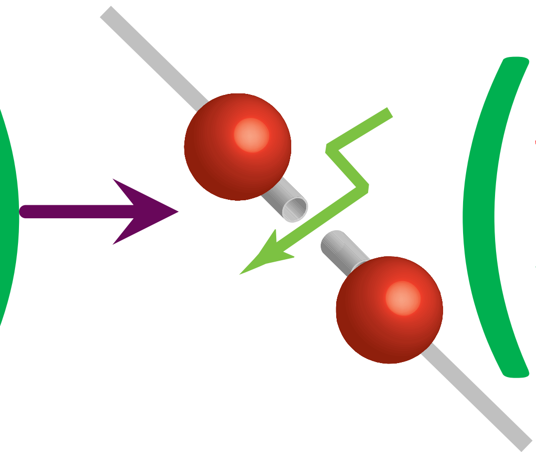

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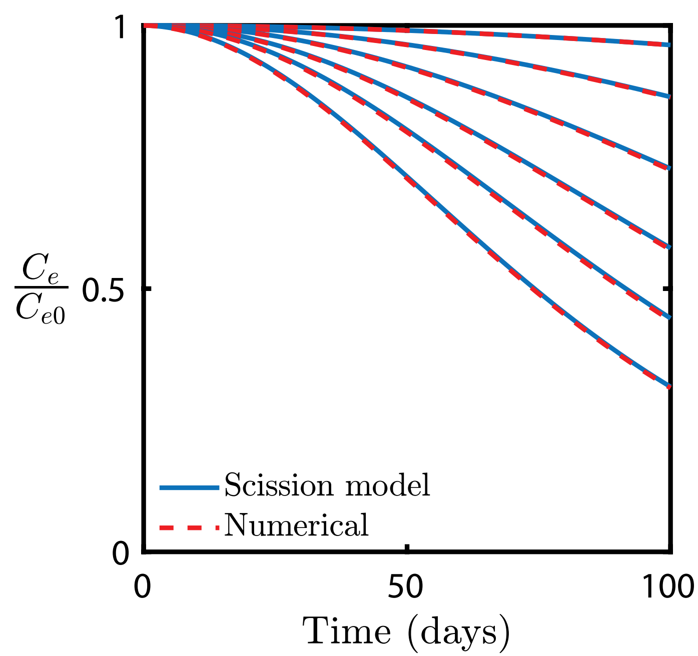
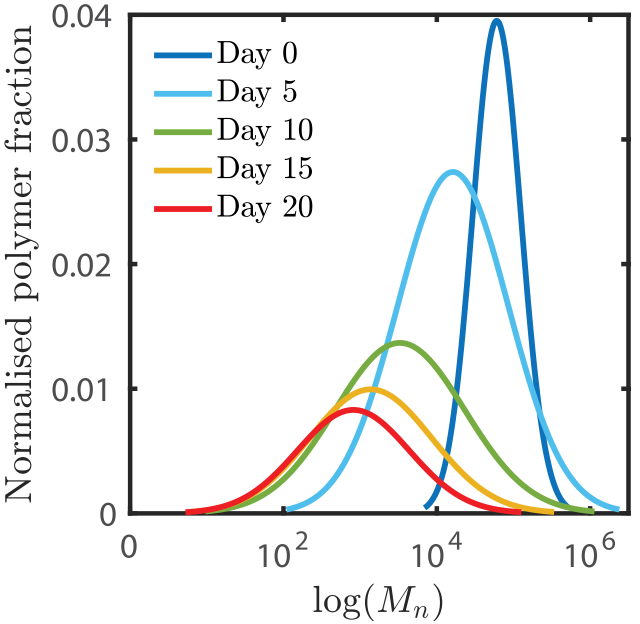


Molecular weight



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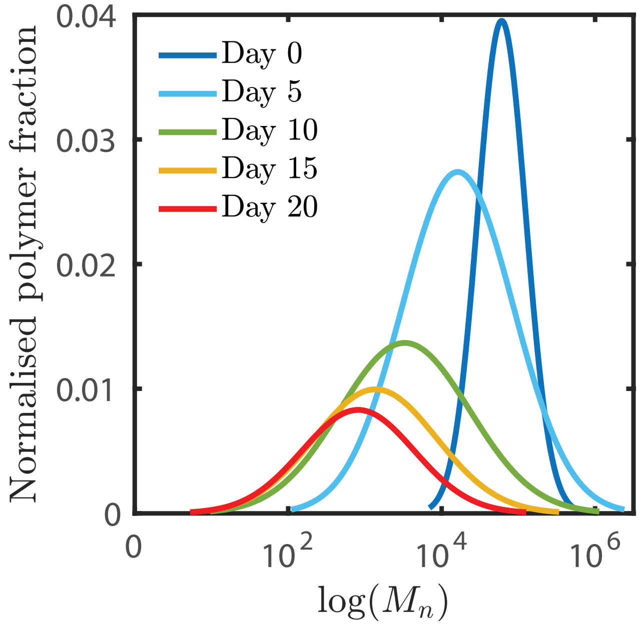

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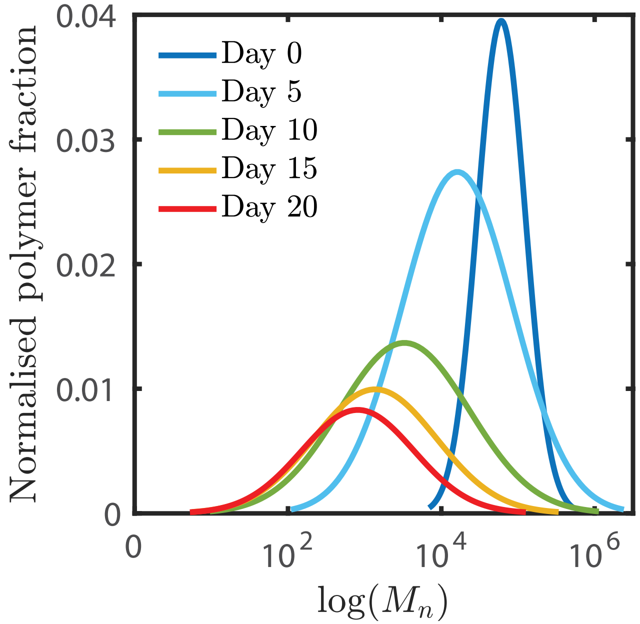

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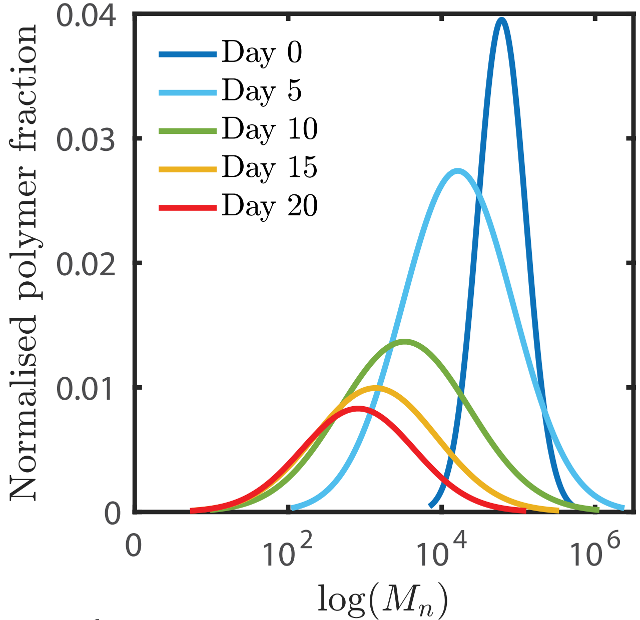

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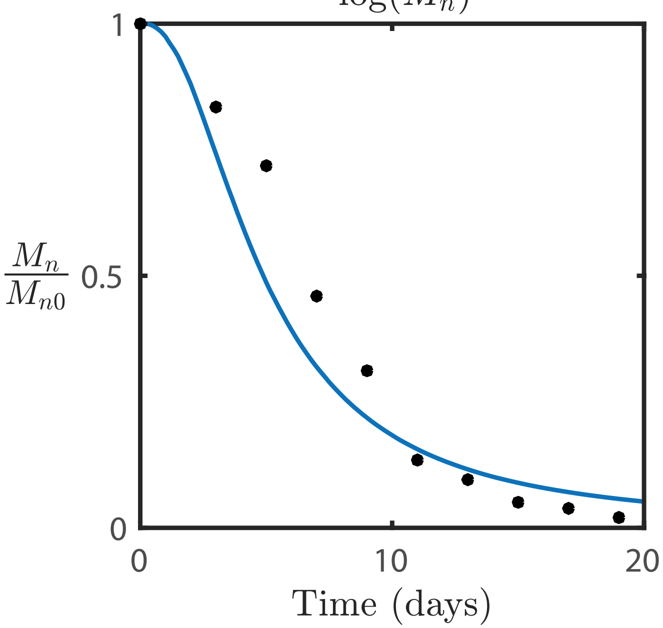

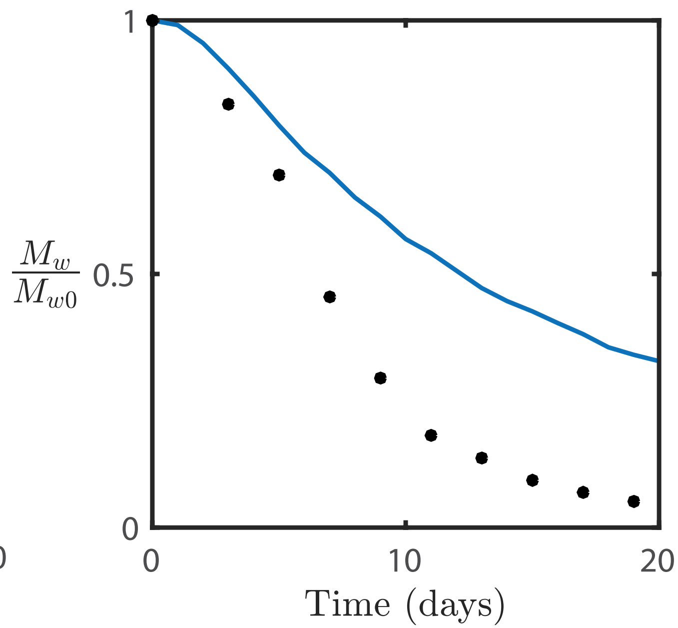

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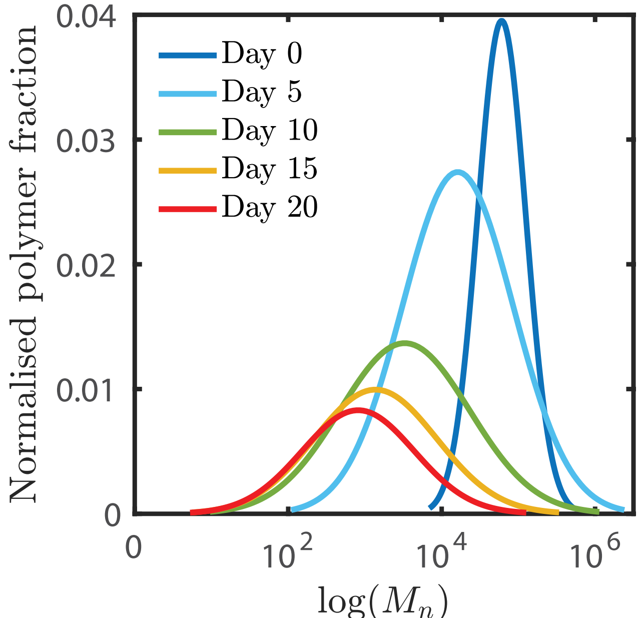

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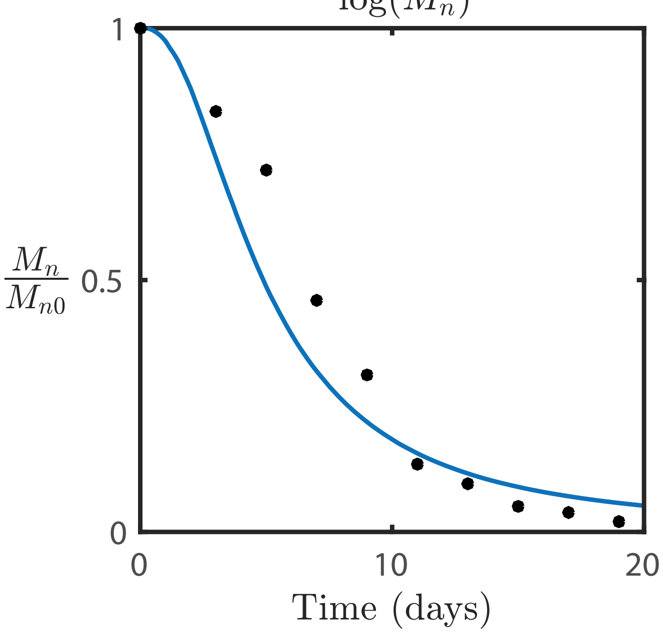

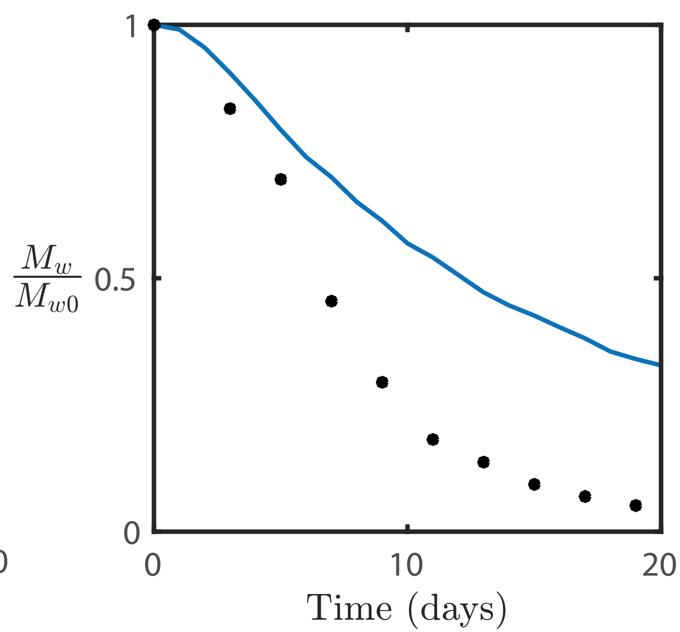

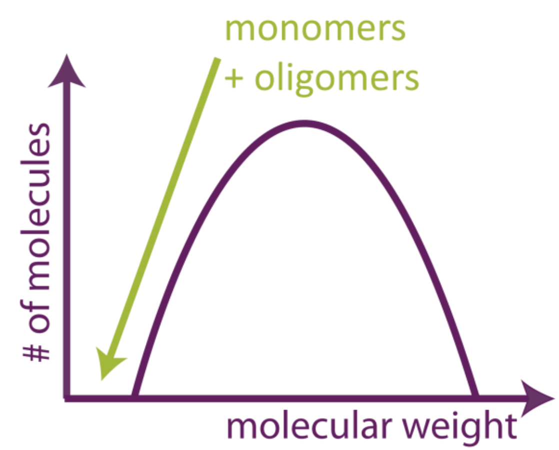

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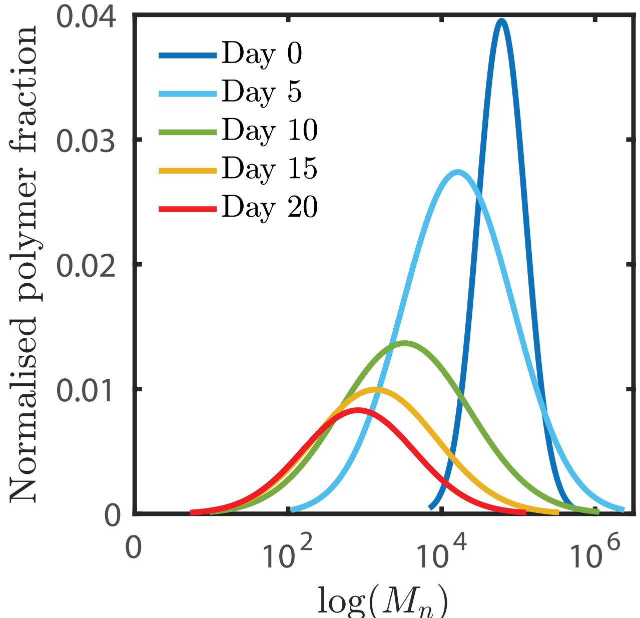

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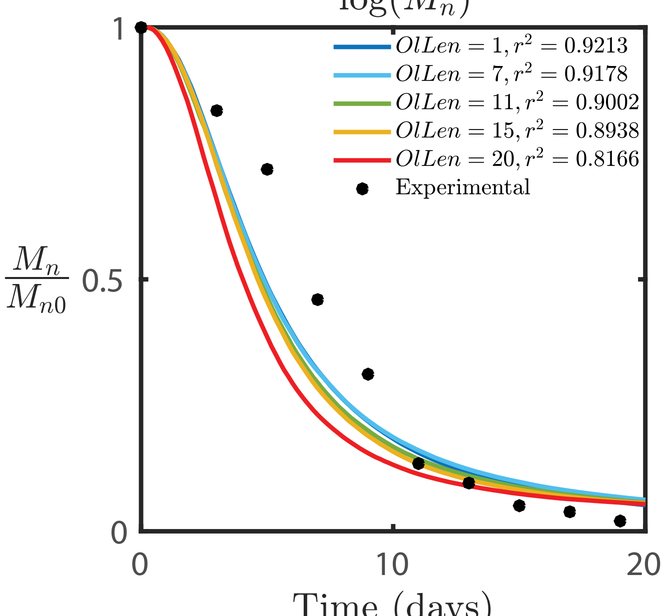

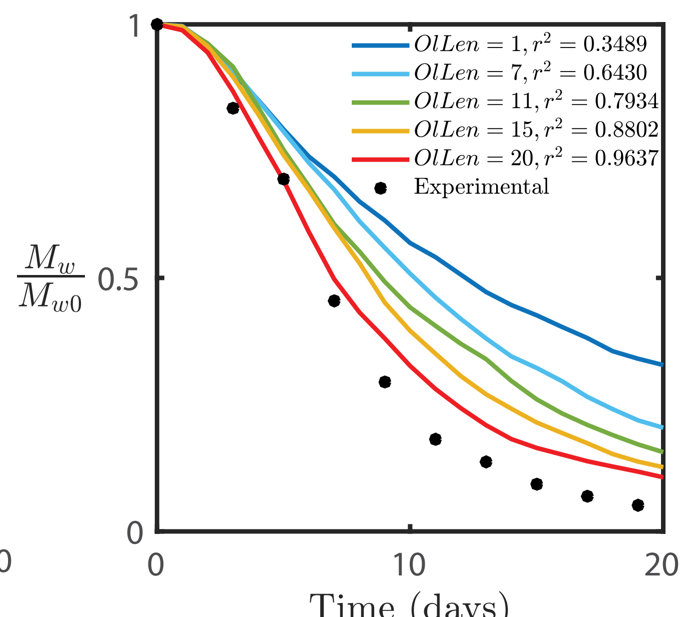

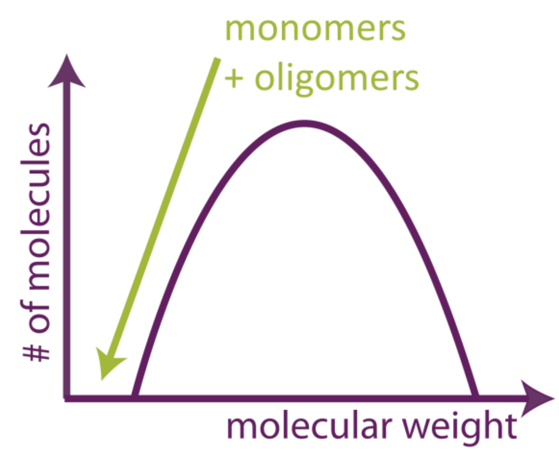

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Young's modulus

$$E = 3NkT$$

N – chains per unit volume
k – Boltzmann's constant
T – absolute temperature

Wang et al., JMBBM, **3**:14-21, 2010.

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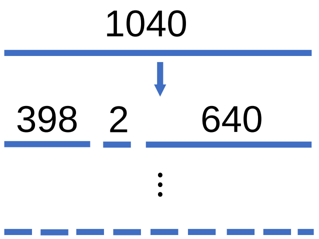

$M = 1040$

$M = 347$

$M < M_{th}$

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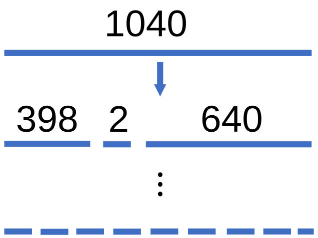

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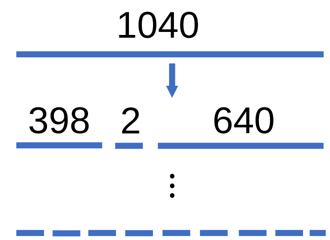

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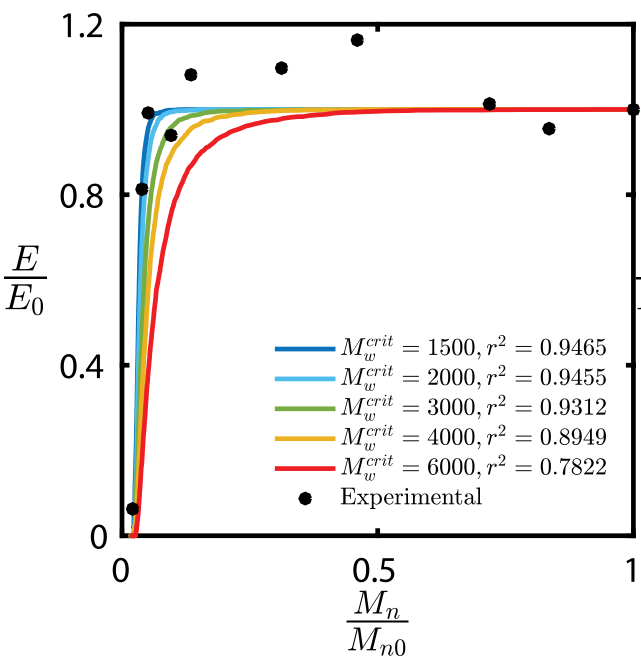

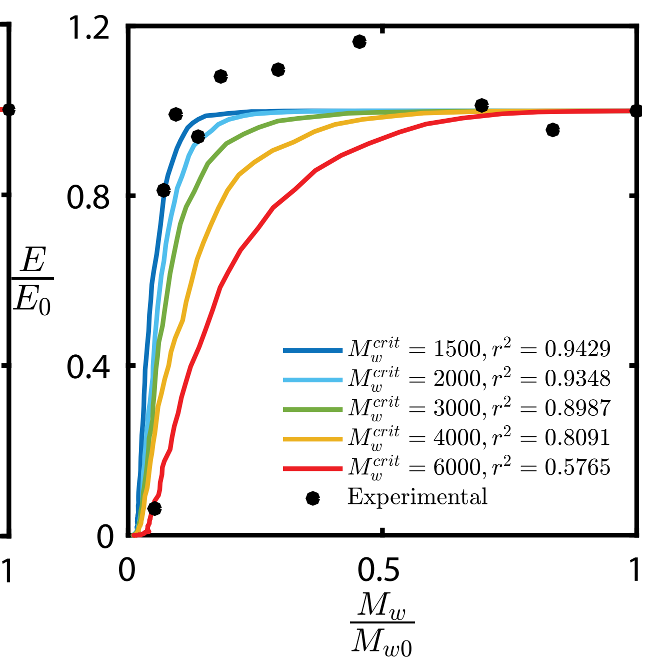

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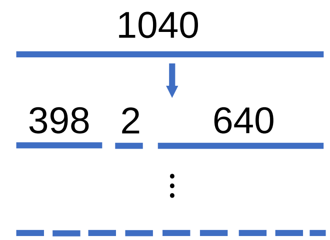

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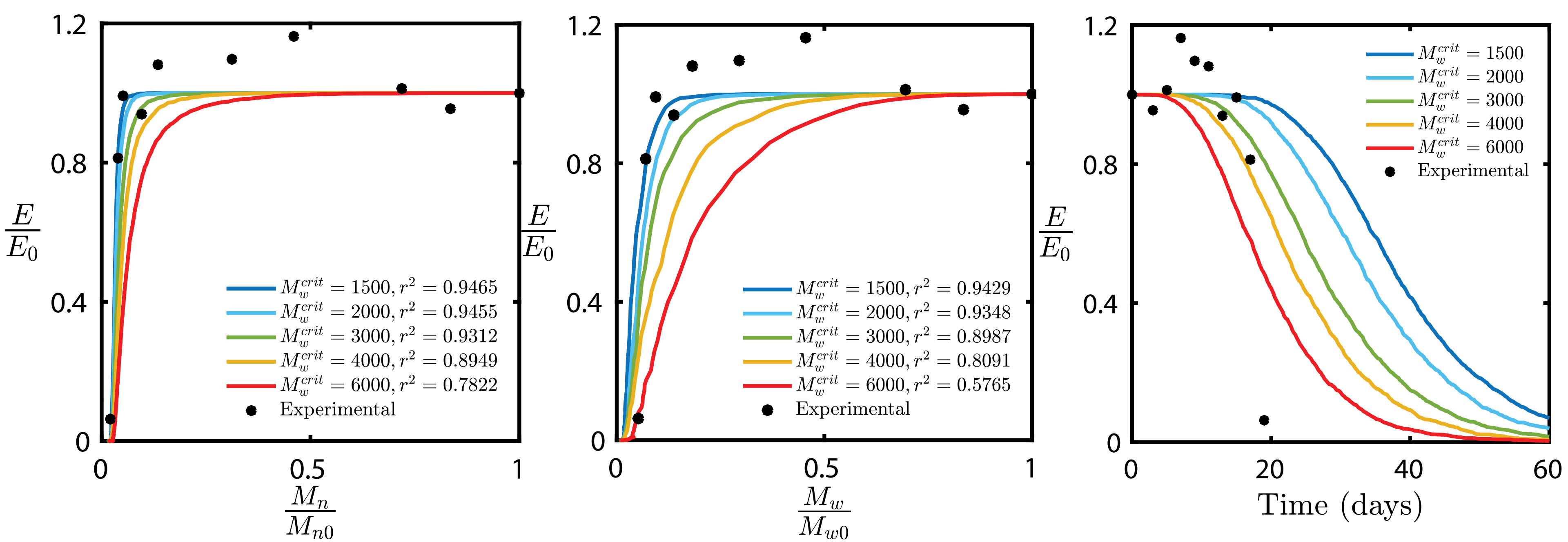

$k_{he} = 1e^{-6}\ \mathrm{day}^{-1}$, $k_{ae} = 1e^{-6}\ (\mathrm{m}^3\mathrm{mol}^{-1})^{0.5}\mathrm{day}^{-1}$, $k_{hr} = 0\ \mathrm{day}^{-1}$, $k_{ar} = 6e^{-6}\ (\mathrm{m}^3\mathrm{mol}^{-1})^{0.5}\ \mathrm{day}^{-1}$, $OlLen = 15$.

Shirazi et al., Acta Biomaterialia, **10**:4695-4703, 2014. Wang et al., JMBBM, **3**:14-21, 2010.

Summary

$$\frac{dC_e}{dt} = -(k_h C_e + k_a C_e C_a^{0.5})$$

$$\frac{dC_m}{dt} = k_h C_e + k_a C_e C_a^{0.5}$$

$$\downarrow$$

$$EndScissions = k_{he} C_e + k_{ae} C_e C_a^{0.5}$$

$$RandomScissions = k_{hr} C_e + k_{ar} C_e C_a^{0.5}$$

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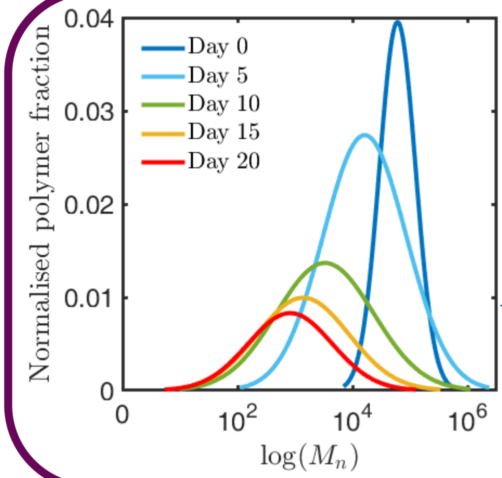

$$M_n = \frac{\sum_{i=1}^{\#chains} N_i M_i}{\sum_{i=1}^{\#chains} N_i}$$

$$M_w = \frac{\sum_{i=1}^{\#chains} N_i M_i^2}{\sum_{i=1}^{\#chains} N_i M_i}$$

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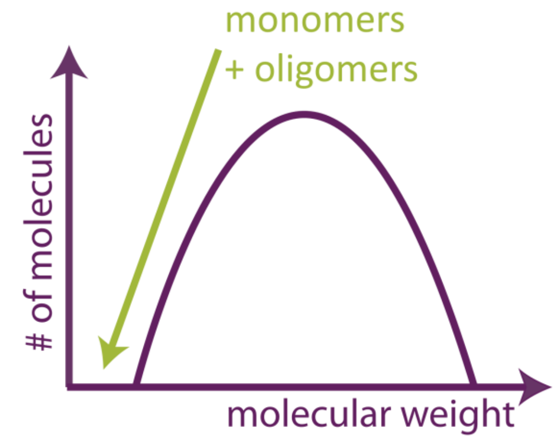

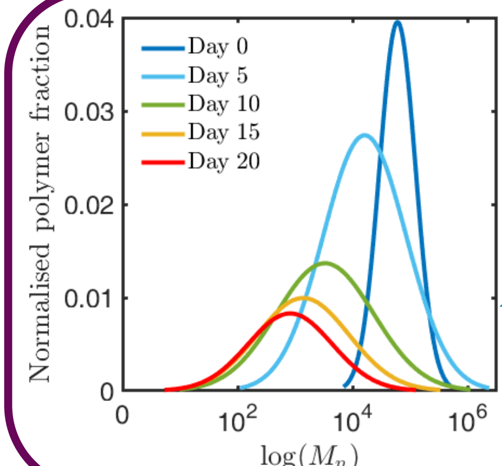

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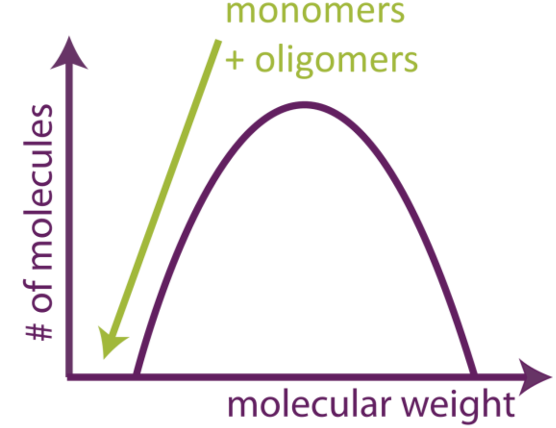
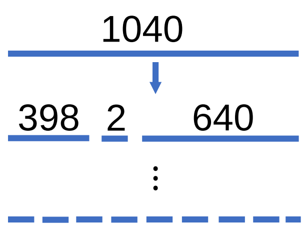


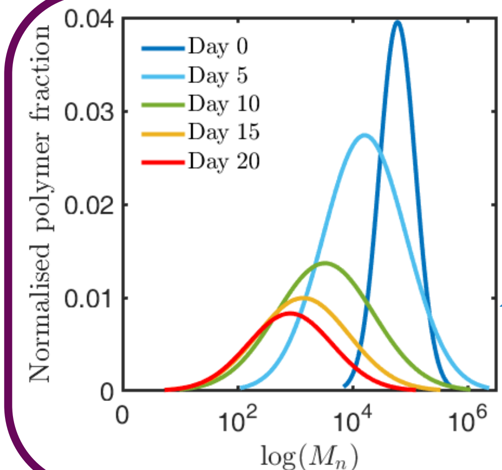
$$2.1\ M_w < M_w^{crit}: N = N - 1$$



$$M = 1040$$

$$M = 347$$

$$M < M_{th} \rightarrow N = N - 1$$



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Summary

$$\frac{dC_e}{dt} = -(k_h C_e + k_a C_e C_a^{0.5})$$

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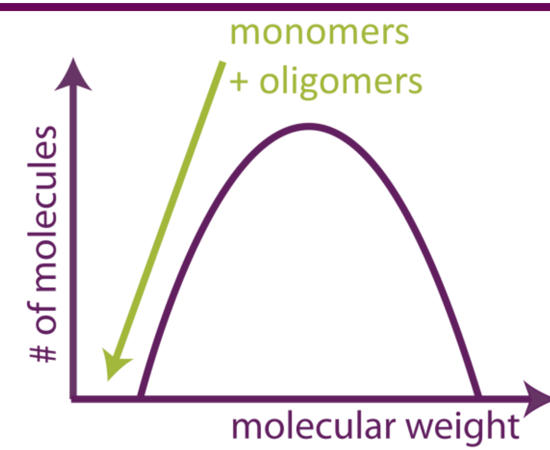


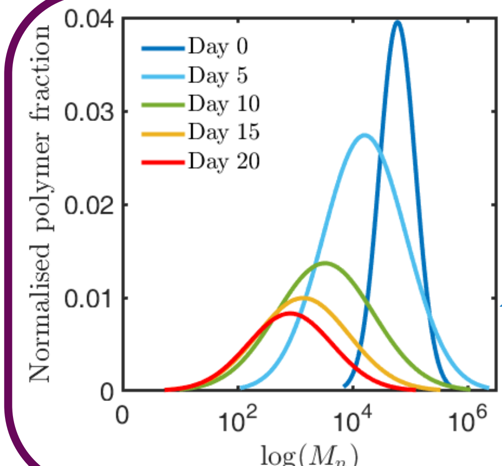
2.1 $M_w < M_w^{crit}: N = N - 1$

1040 — $M = 1040$

398 2 640 — $M = 347$

⋮

$M < M_{th} \rightarrow N = N - 1$



$$M_n = \frac{\sum_{i=1}^{\#chains} N_i M_i}{\sum_{i=1}^{\#chains} N_i}$$

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- Further develop predictions for mechanical properties
- Link to continuum finite element models