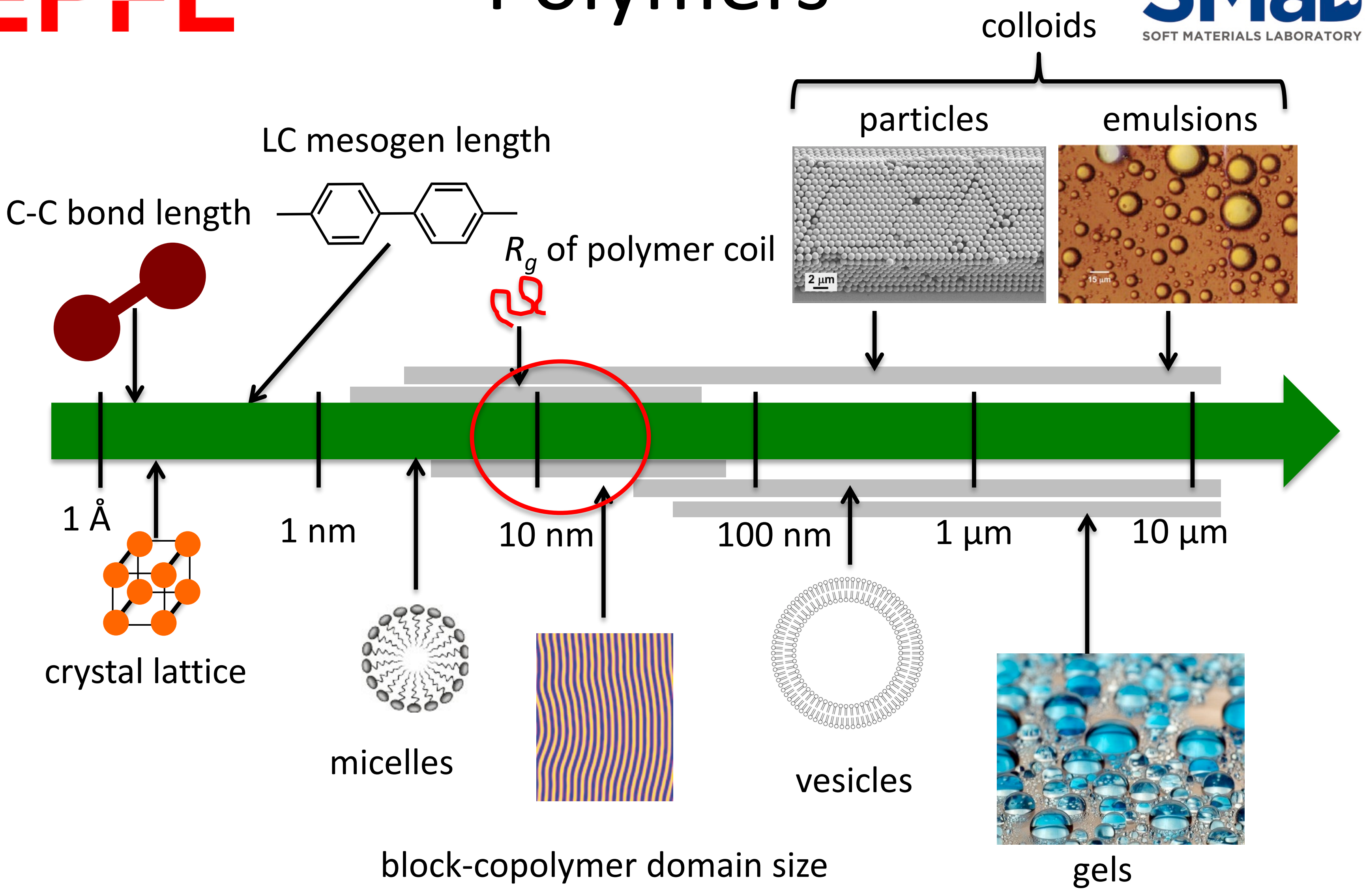
Polymers



colloids

particles

emulsions

LC mesogen length

C-C bond length

R_g of polymer coil

1 Å

1 nm

10 nm

100 nm

1 µm

10 µm

crystal lattice

micelles

vesicles

block-copolymer domain size

gels

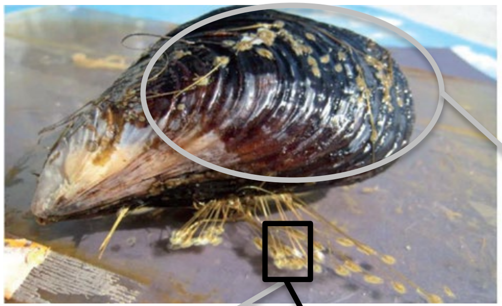
Challenges

14.12.2022: Groups 6, 7, 8, 9, 10, 12
21.12.2022: Groups 14, 16, 20, 23, 25

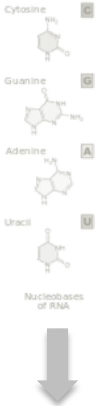
Presentation:
Maximum 10 min + 5 min questions, each team member must present a part

Note that there is NO report to be handed in.

Course outline

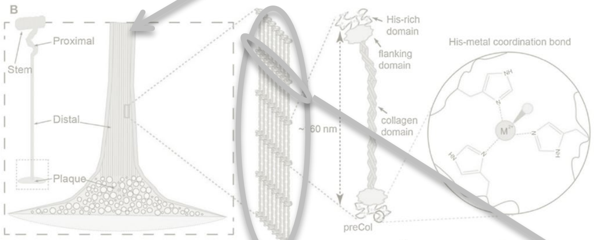


Introduction



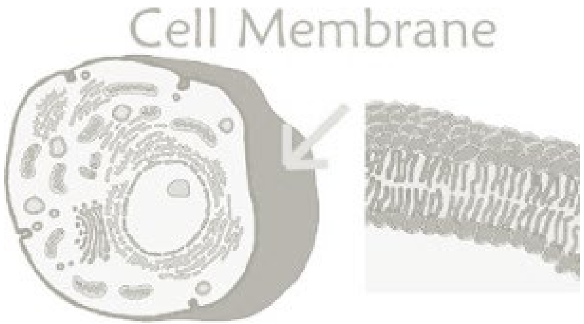
Ordered materials

Thermotropic liquid crystals



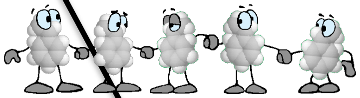
E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

Lyotropic liquid crystals

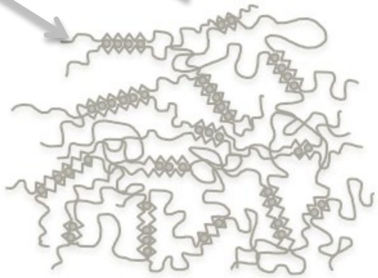


Disordered materials

Polymers

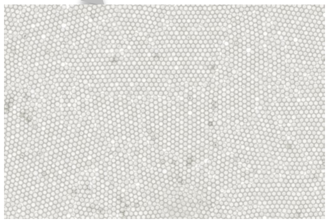


Gels



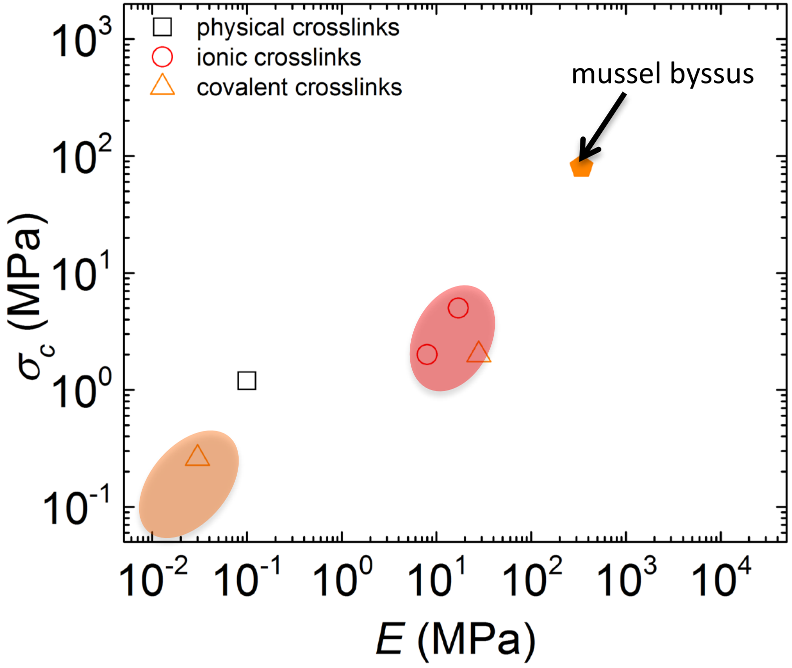
Colloids

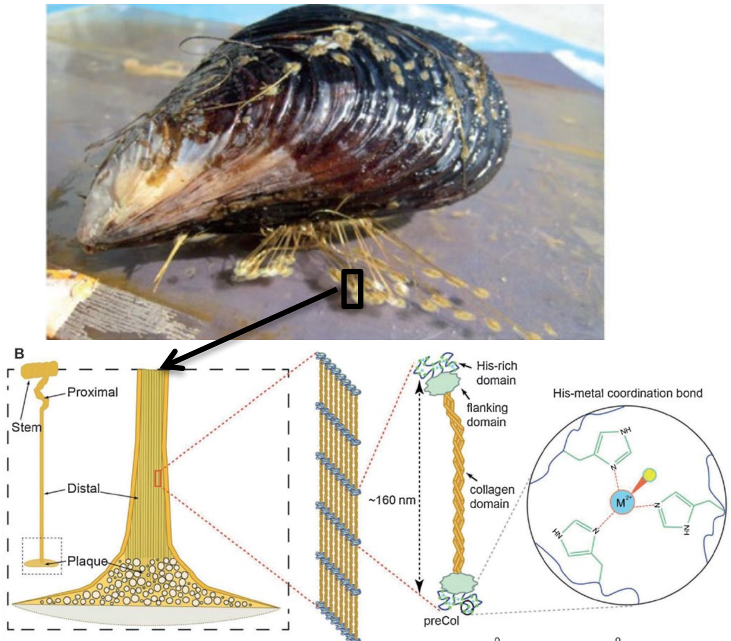
Nanoparticles



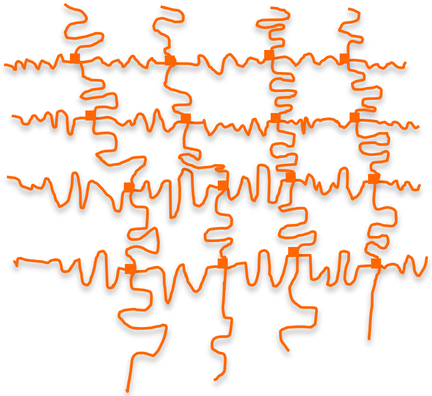
Emulsions

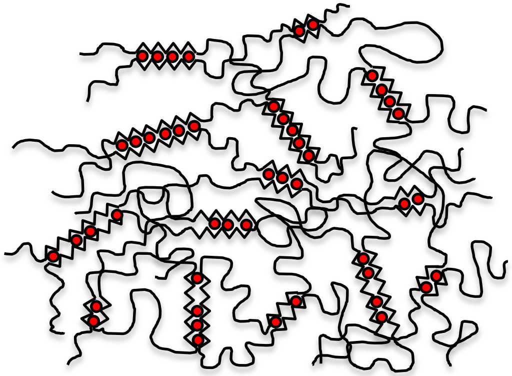
Tough and strong soft materials





E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044





Outline

- Introduction
  - Isomerism
  - Tacticity
- Influence of polymer structure on crystallinity
- Polymer solutions
- Polymer melts
- Polymers
  - Thermoplasts
  - Thermosets
  - Elastomers
- Recycling of polymers
- Characterization of polymers
- Application

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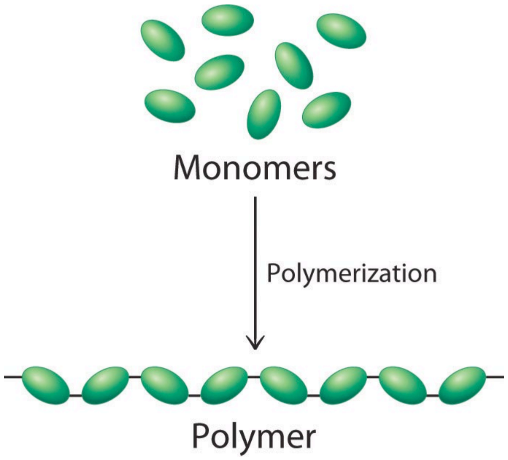
Polymers

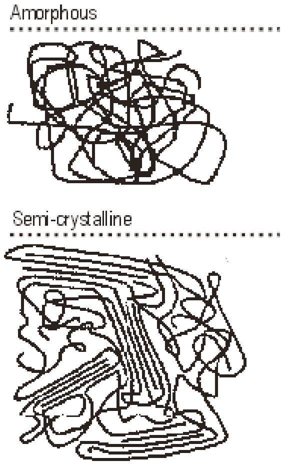
How to make polymers



1. Polymer chemistry and macromolecular engineering: Harm-Anton Klok

2. Organic electronic materials: Holger Frauenrath

How do they arrange?

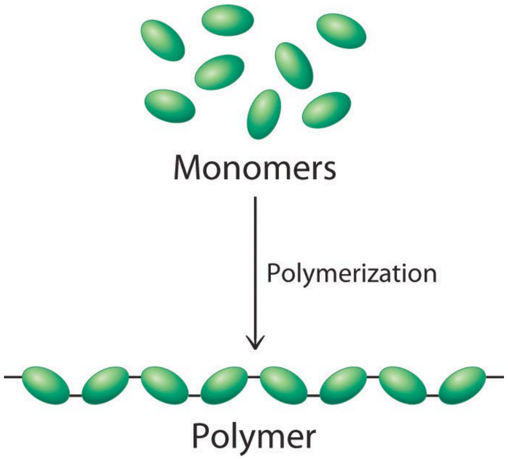


Physical chemistry of polymeric materials: Eva Klok-Lermann

How can we make gels?

Polymers

How to make polymers



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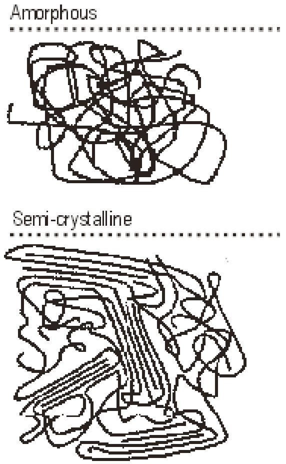
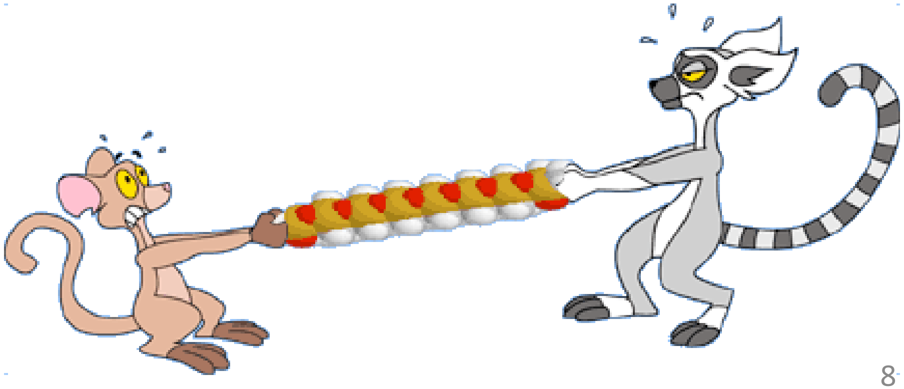
How do they arrange?



How can we make gels?

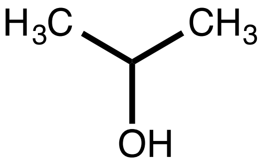
How does the structure influence their properties?



Isomerism

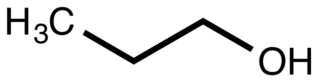
Isomers are molecules that have the same chemical formula but different structures.

Example 1: C_3H_7OH



isopropanol

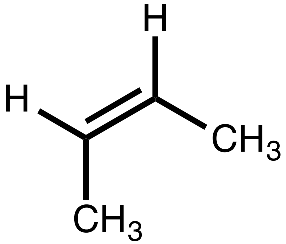
T_m = -89°C
T_b = 83 °C
η at 25°C = 1.96 mPas



1-propanol

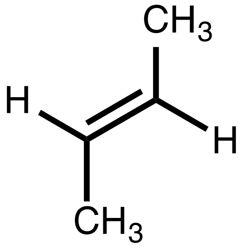
T_m = -126°C
T_b = 97 °C
η at 25°C = 1.96 mPas

Example 2: C_4H_8



cis-2-butene

T_m = -139°C
T_b = 4 °C



trans-2-butene

T_m = -106°C
T_b = 4 °C

Why does isopropanol have a much higher melting temperature than 1-propanol?

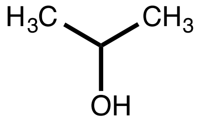
A. Stronger VdW forces

B. More H-bonds

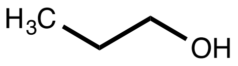
C. It is easier to be packed into a crystal structure

D. All of the above answers

isopropanol



1-propanol



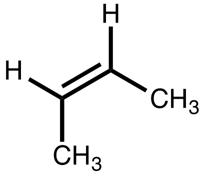
Why are the boiling points of cis- and trans-butene the same?

A. VdW forces between molecules are equally strong.

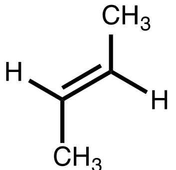
B. They are equally easily packed into a crystal structure.

C. They have equal vapor pressures.

cis-2-butene



trans-2-butene



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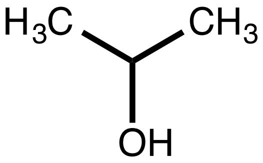

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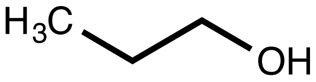

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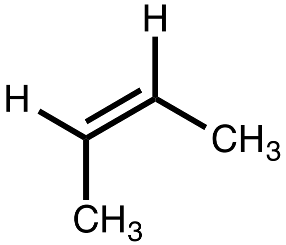
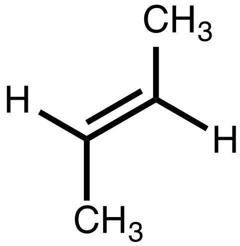


cis-2-butene

T_m = -139°C
T_b = 4 °C

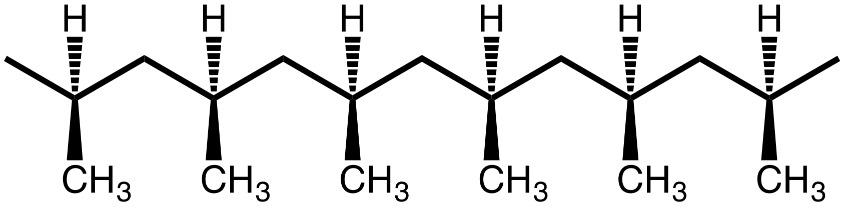


trans-2-butene

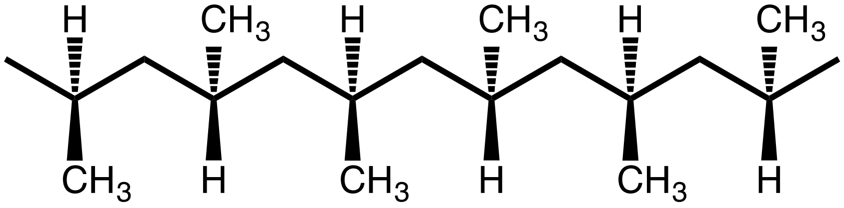
T_m = -106°C
T_b = 4 °C

Tacticity

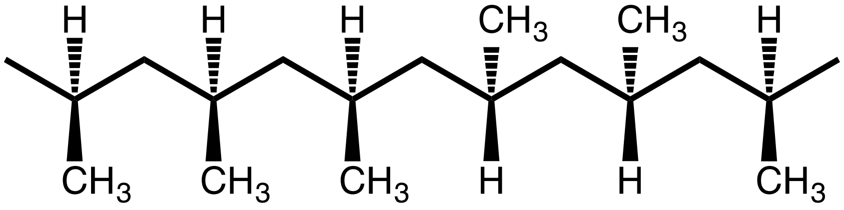
Example: poly(propylene)



isotactic



syndiotactic



atactic

The tacticity influences the ability and propensity of polymers to crystallize.

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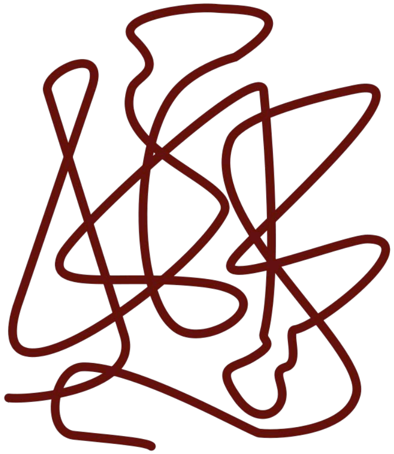
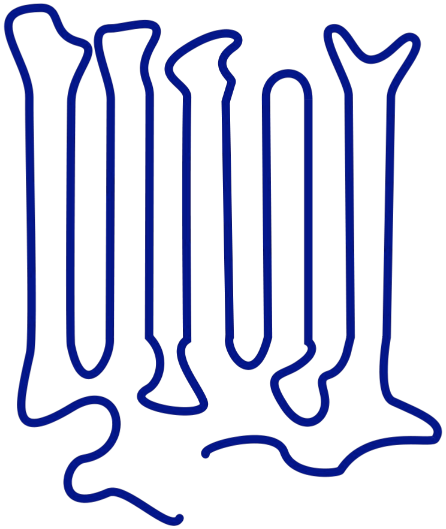
Polymer structure

most polymers are amorphous

Polymers can crystallize if chains are stretched ➔ this is entropically very expensive ➔ there are always some chain ends that coil and thus result in amorphous areas.



Amorphous



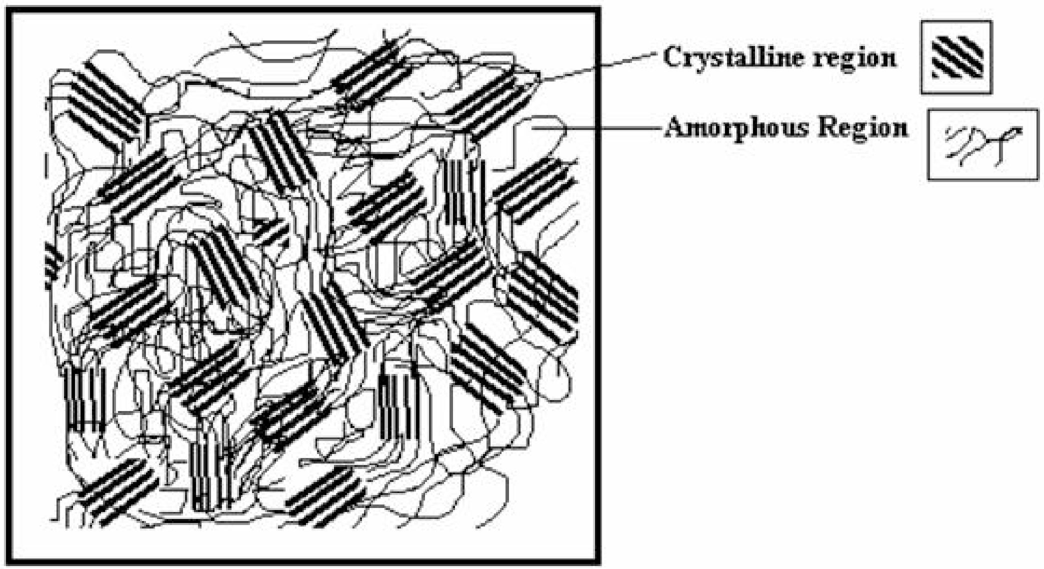
Semicrystalline

What determines the propensity of polymers to crystallize?

Propensity of polymers to crystallize

Typically, the propensity of polymers to crystallize is higher if they

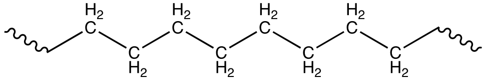
- have rigid straight chains, side chains, or blocks
- have regularly spaced side groups
- are isotactic (compared to atactic polymers)



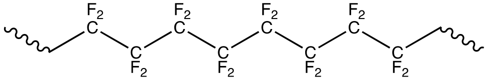
http://www.engr.utk.edu/mse/Textiles/Polymer%20Crystallinity.htm

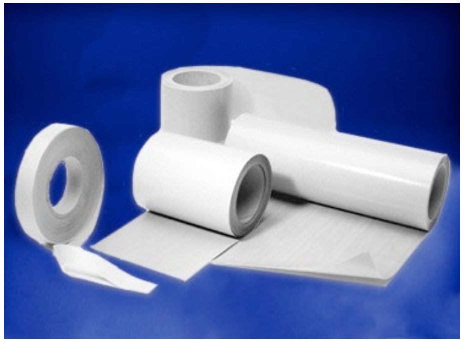
Examples of semi-crystalline polymers

linear poly(ethylene)

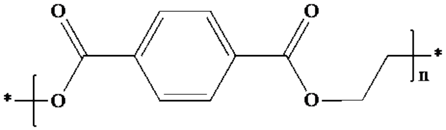


poly(tetrafluoroethylene)





poly(ethylene terephthalate)



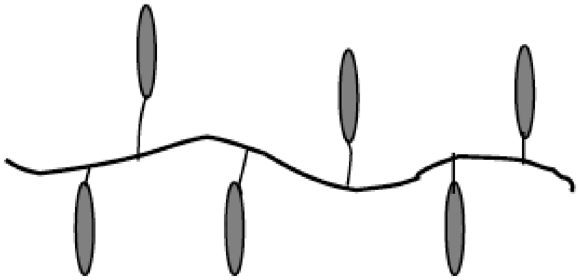
Liquid crystalline polymers

Main-chain liquid crystal polymers

- The main chain contains liquid crystals.
- If the polymer has side chains, they are flexible.

Side-chain liquid crystal polymers

side chain side-on



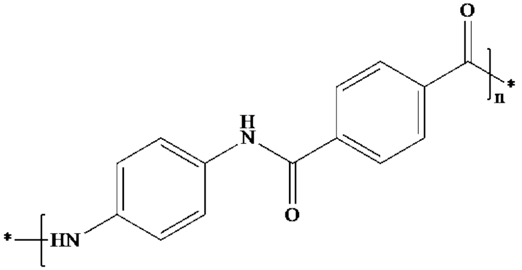
side chain end-on

- The main chain is flexible.
- The side chains are composed of or contain liquid crystals.

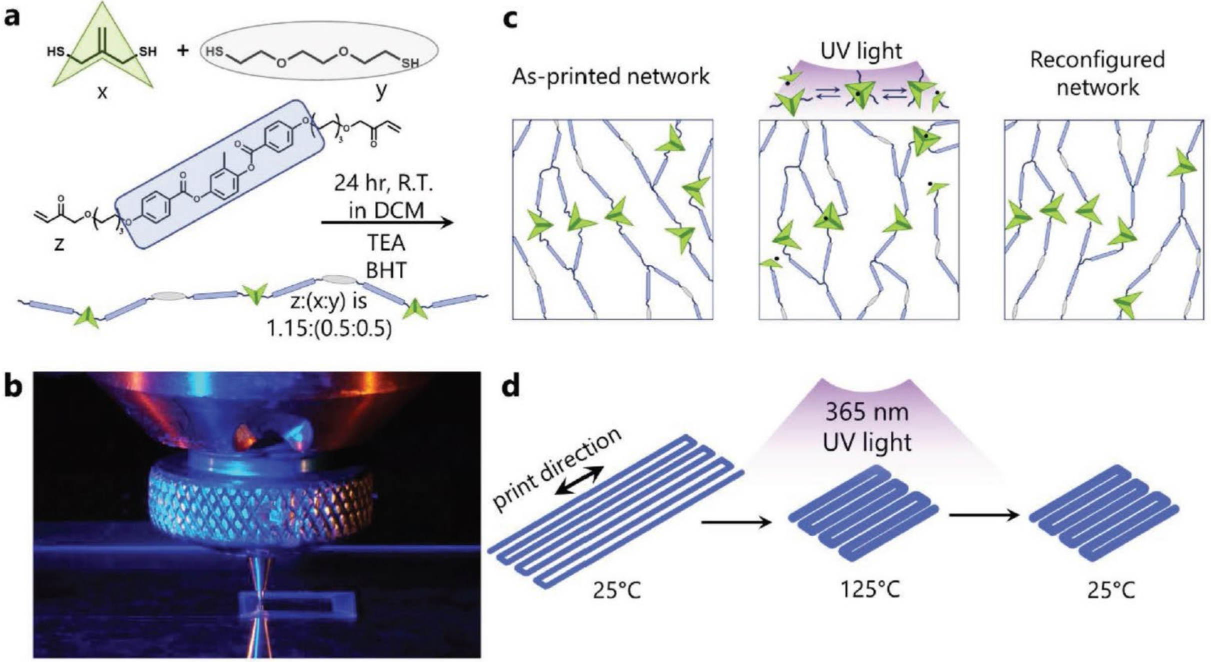
Li, M.-H.; Keller, P. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* **2006**, *364*, 2763

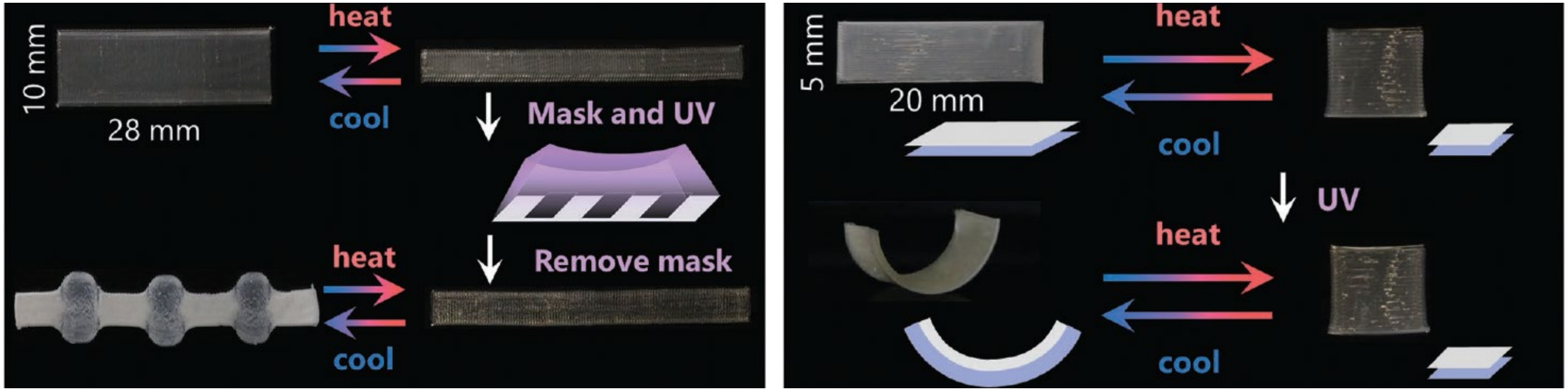
Examples of liquid crystalline polymers

Kevlar



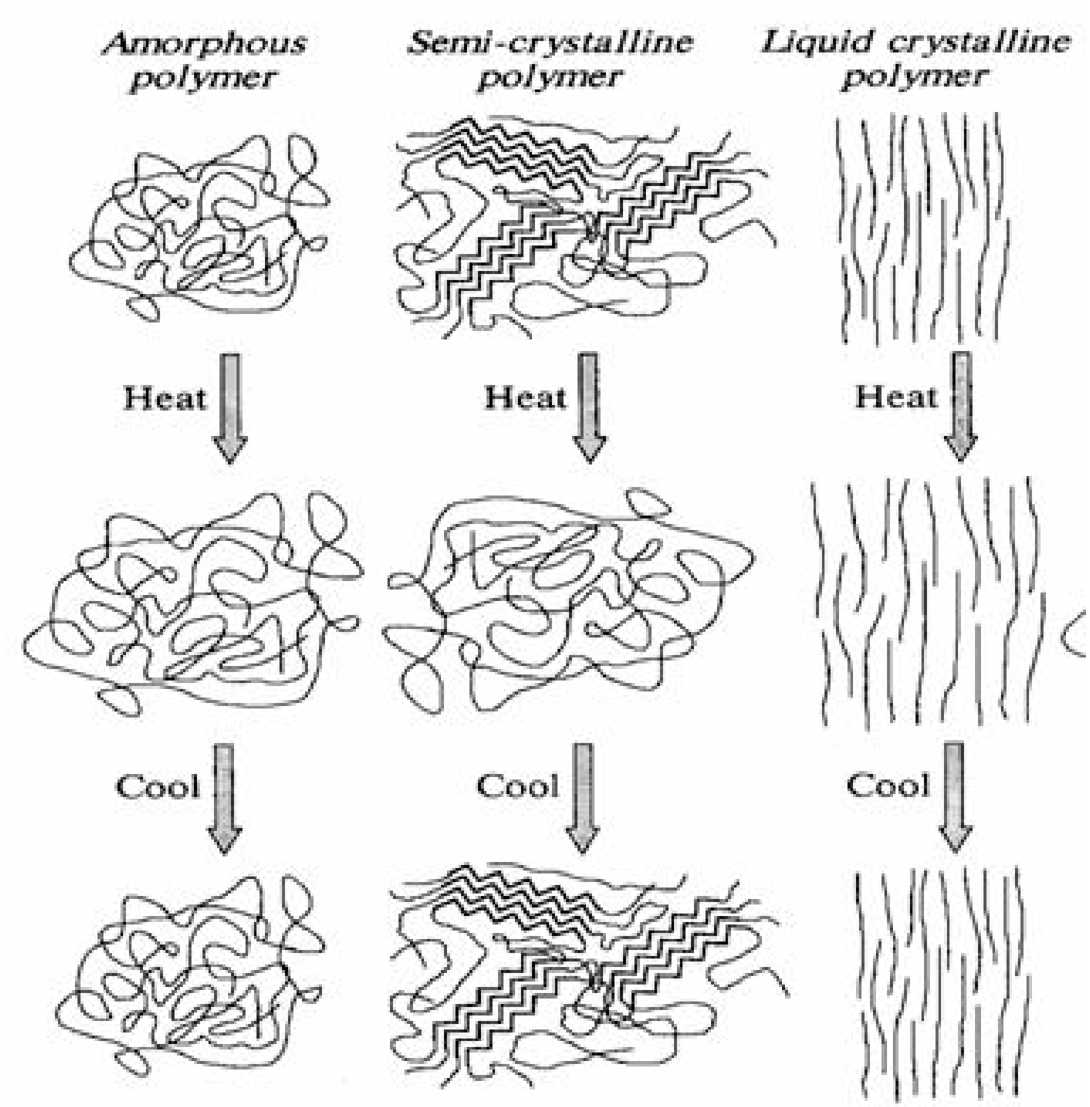
Recap: Shape memory materials





Davidson, E. C. *et al., Advanced Materials* **2020**, *32* (1), 1905682.

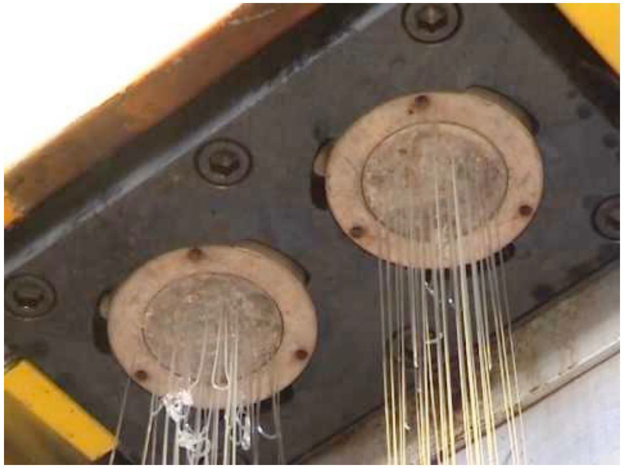
T-dependent polymer structures



http://www.imould.com/news/plastic+injection+mold+Molecular+Weight+and+Mechanical+Properties-1910.html

Processing of polymers

from melts



from solutions

Processing of polymers in nature

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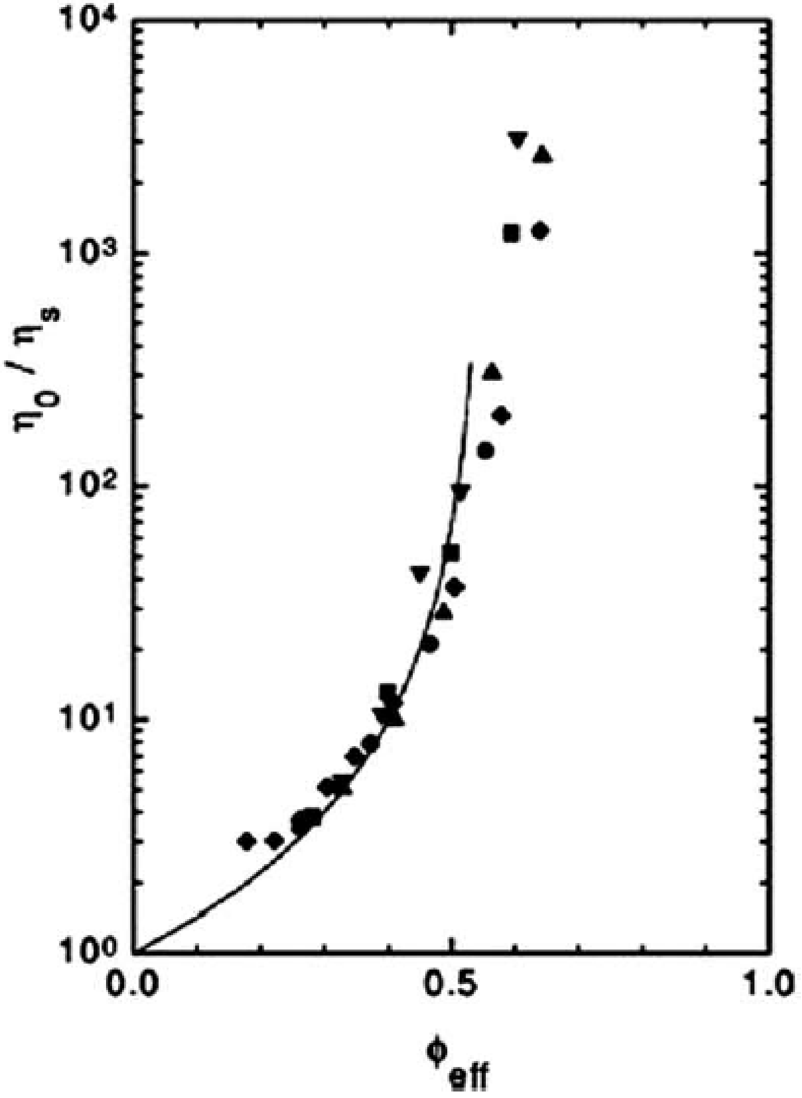
What happens to the viscosity of a solution if polymers are added?

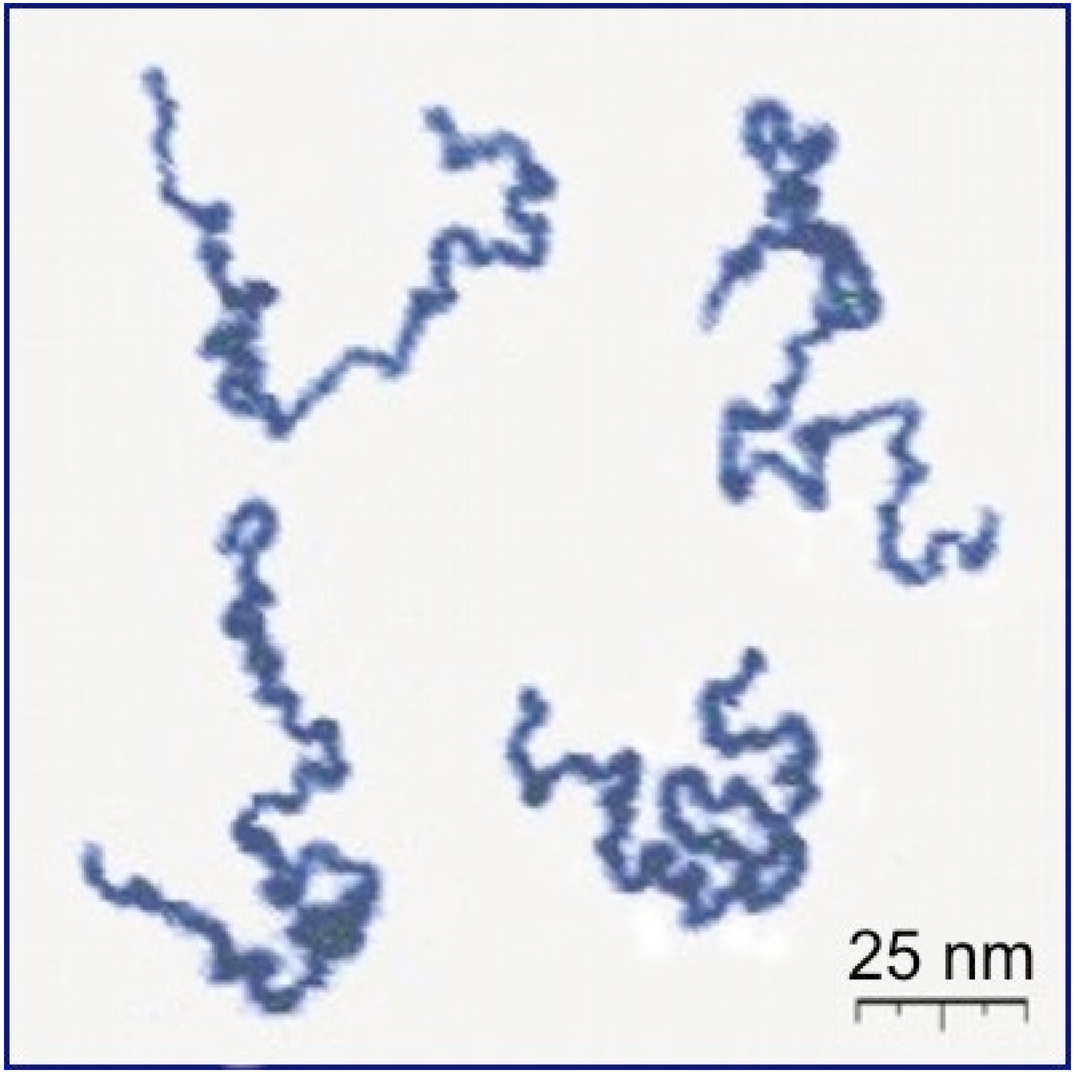
A. It remains unchanged.
B. It decreases with increasing polymer concentration.
C. It increases with increasing polymer concentration.
D. It starts behaving as a Newtonian fluid.

Viscosity of polymer solutions



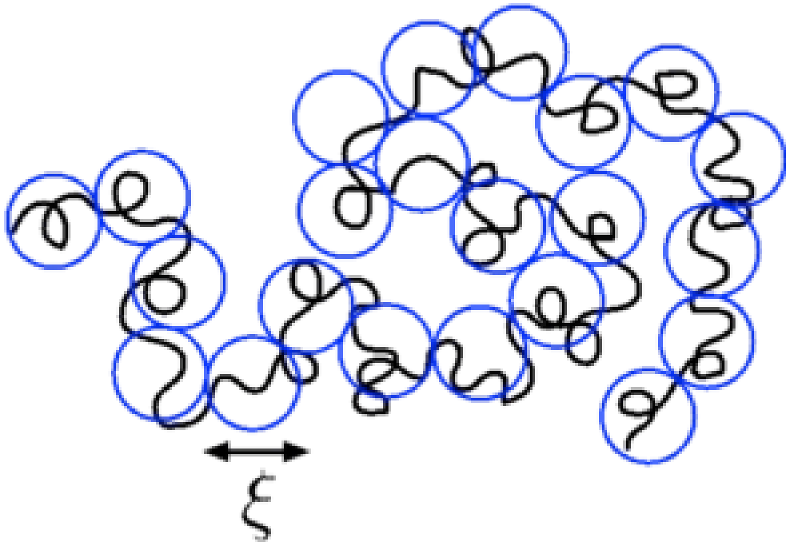
H. Senff and W. Richtering, *Journal of Chemical Physics*, 1999, **111**, 1705-1711

Dimensions of a polymer

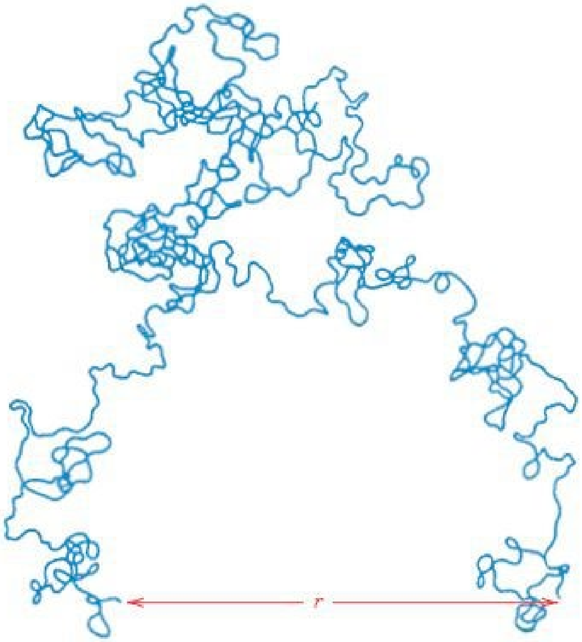


Ideal chains

The simplest way to describe a polymer is to assume that its individual segments undergo random walk and do not interact with each other. This description is called the **Gaussian limit**.

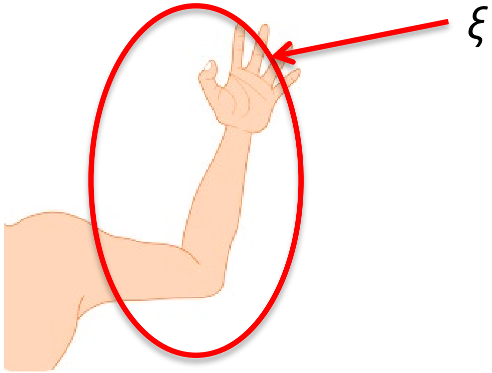


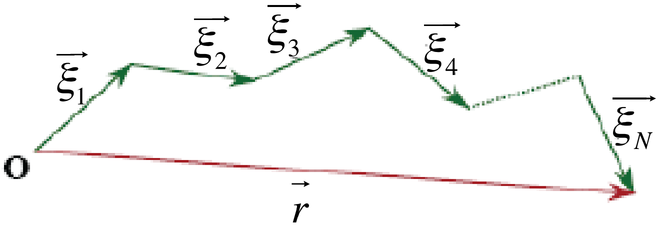
http://www.eng.yale.edu/polymers/docs/classes/polyphys/lecture_notes/3/handout3_wse3.html



https://capolight.wordpress.com/2010/06/14/a-brief-explanation-of-polymers/

Gaussian limit: Kuhn length





ξ: Kuhn length [m]
a: persistence length [m]
N: number of repeat “units” [-]
R_g: radius of gyration [m]
r: end-to-end distance [m]

$$\vec r = \vec\xi_1 + \vec\xi_2 + \ldots + \vec\xi_N = \sum_{i=1}^{N} \vec\xi_i$$

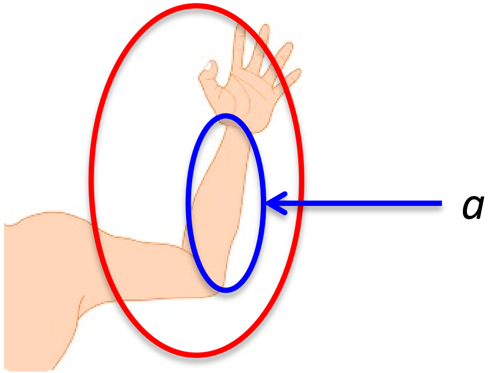
$$\left\langle \vec r \vec r \right\rangle = \left\langle \left(\sum_{i=1}^{N} \vec\xi_i\right)\left(\sum_{i=1}^{N} \vec\xi_i\right)\right\rangle$$

$$\left\langle \vec r^{\,2} \right\rangle = \left\langle \sum_i \sum_j \vec\xi_i \vec\xi_j \right\rangle = N\xi^2 + \sum_{i\neq j} \vec\xi_i \vec\xi_j$$

for ideal chains and theta solvents:

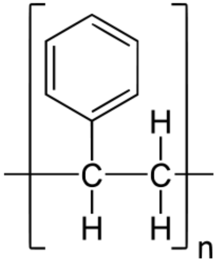
$$\left\langle r^2 \right\rangle = N\xi^2$$

Gaussian limit: persistent length



$$\langle r^2 \rangle = N\xi^2$$

What about poly(styrene) who has a restricted bond angle Φ?



ξ: Kuhn length [m]
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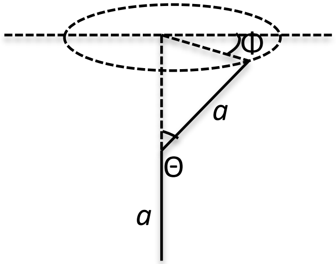
Schematic illustration of a section of a polymer chain:



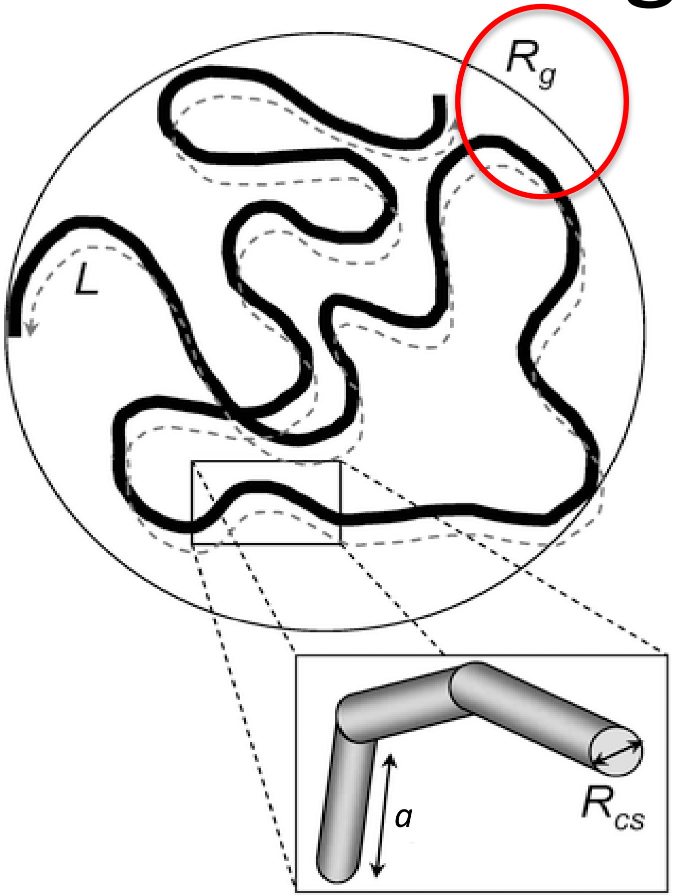
For freely rotating chains in theta solvents (no restrictions on Φ):

$$\langle r^2 \rangle_0 = Na^2 \left(\frac{1 + cos\theta}{1 - cos\theta} \right)$$

For hindered rotating chains in theta solvents (with a restricted bond angle Φ):

$$\langle r^2 \rangle_0 = Na^2 \left(\frac{1 + cos\theta}{1 - cos\theta} \right) \left(\frac{1 - \langle cos\phi \rangle}{1 + \langle cos\phi \rangle} \right)$$

Additional length scales



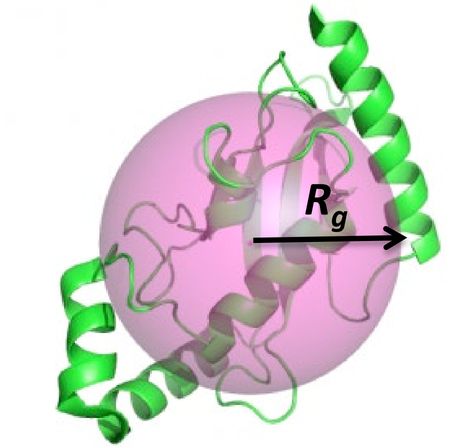
C. A. Dreiss, *Soft Matter* **3**, 956 (2007)

L: contour length [m]
a: persistence length [m]
N: number of repeat “units” [-]
R_g: radius of gyration [m]

contour length: $L = Na$

Radius of gyration, R_g

The radius of gyration is the distance from the mass center of an object with mass *m*, that gives an equivalent inertia (with mass *m*) if the object is spherical.



http://www.pymolwiki.org/index.php/Radius_of_gyration

For an ideal chain, the segments around the center of mass have a Gaussian distribution. Ideal chains are thus often referred to as Gaussian chains.

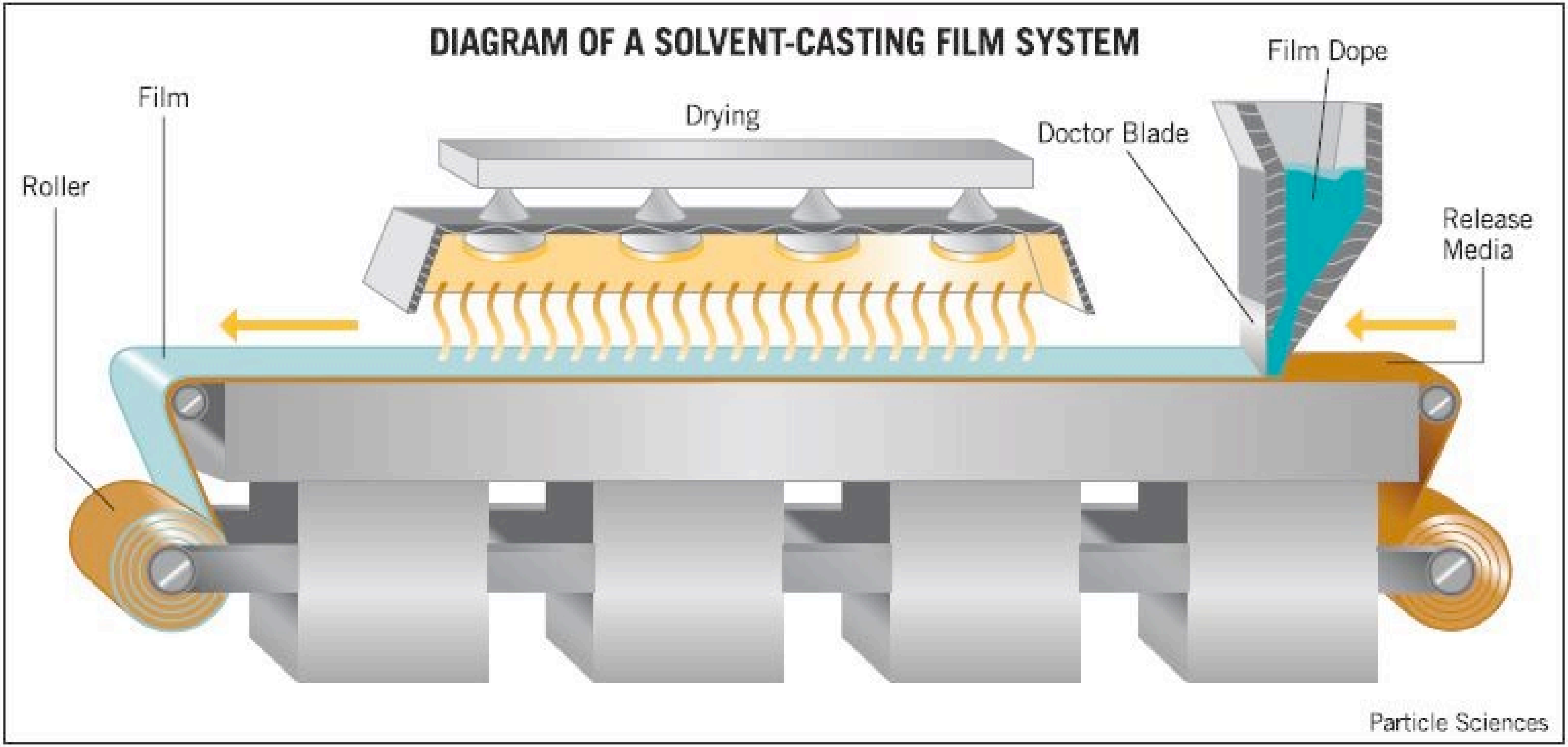
$$\sqrt{\left\langle R_g^2 \right\rangle} = \sqrt{\frac{a^2 N}{6}} = \sqrt{\frac{\left\langle r^2 \right\rangle_0}{6}}$$

Which length scale do you use to calculate the volume fraction of polymers in solution?

A. persistence length
B. Kuhn length
C. radius of gyration
D. end-to-end distance
E. contour length

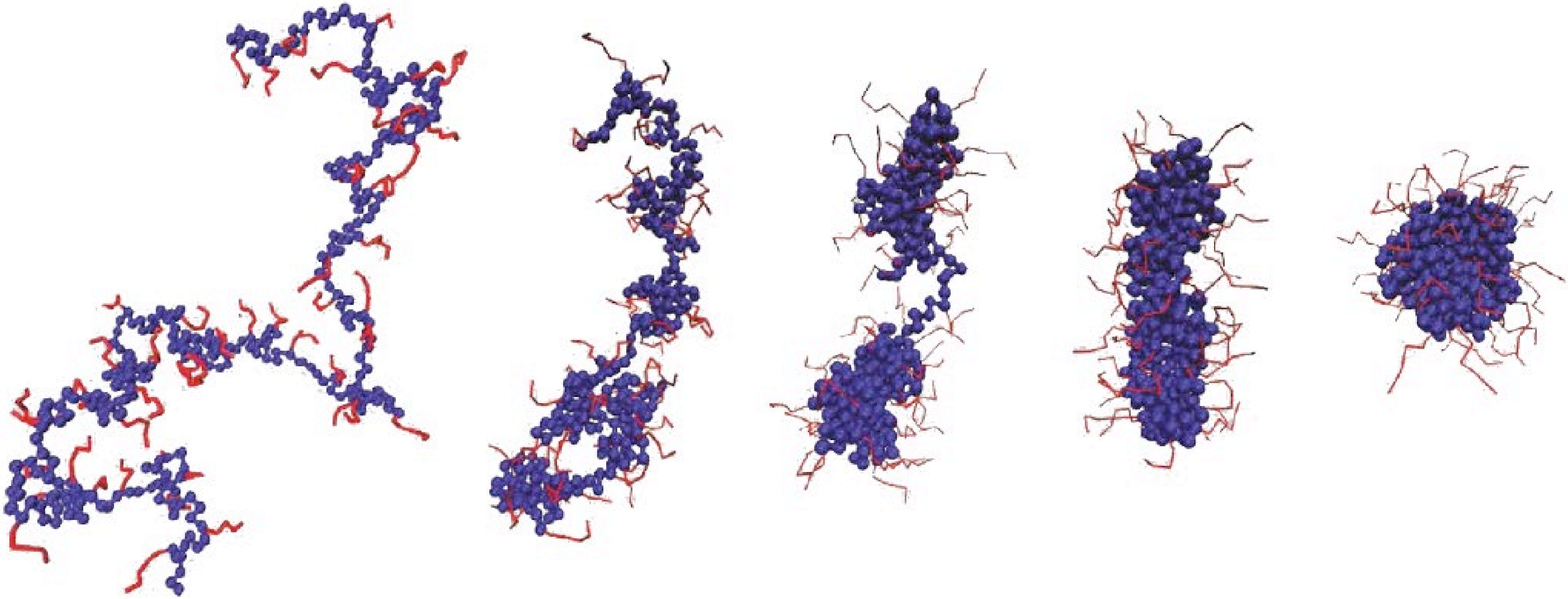
Polymer solutions

Figure 1



http://www.particlesciences.com/news/technical-briefs/2010/dissolving-films.html

Polymers in solution



K. I. Popov, V. V. Palyulin, M. Möller, A. R. Khokhlov and I. I. Potemkin, *Beilstein Journal of Nanotechnology*, 2011, **2**, 569-584.

Solvent quality

The solvent quality is a measure for the interactions between polymer repeat units and the solvent molecules.

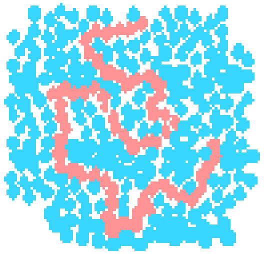
Good solvent:
Solute-solvent interactions are favored such that the chain is swollen.

Theta solvent:
The interactions between different solute molecules are equal to those between solutes and solvents.

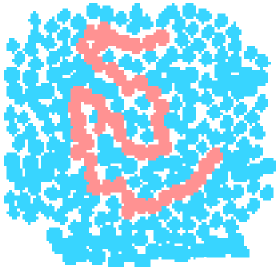
Poor solvent:
The solute-solute interactions are favored such that the chain is contracted.

Interaction parameter:

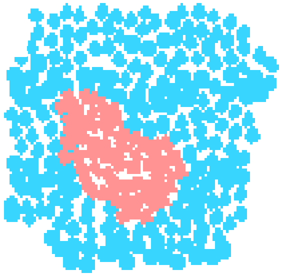
$\chi < 0.5$



$\chi = 0.5$



$\chi > 0.5$



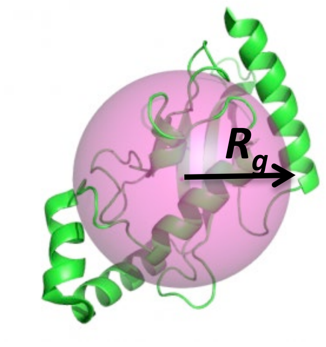
How does the solvent quality influence the end-to-end distance of polymers?

$$\sqrt{\langle r^2 \rangle} \propto N^{\upsilon}$$

good solvent: $\upsilon = 0.588$
theta solvent: $\upsilon = 0.5$
poor solvent: $\upsilon = \frac{1}{3}$

υ: Flory exponent [-]
χ: interaction parameter [-]

Influence of solvent on polymer dimensions



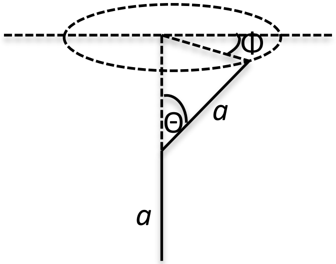
http://www.pymolwiki.org/index.php/Radius_of_gyration

For chains with no steric restrictions:

$$\sqrt{\langle R_g^2 \rangle} = \sqrt{\frac{\langle r^2 \rangle}{6}} = \frac{N^{\nu} a}{\sqrt{6}}$$

a: persistence length [m]
N: number of repeat "units" [-]
R_g: radius of gyration [m]

For chains with steric restrictions:



For freely rotating chains (no restrictions on Φ):

$$\sqrt{\langle r^2 \rangle} = N^{\nu} a \sqrt{\left(\frac{1 + cos\theta}{1 - cos\theta}\right)}$$

For hindered rotating chains (with a restricted bond angle Φ):

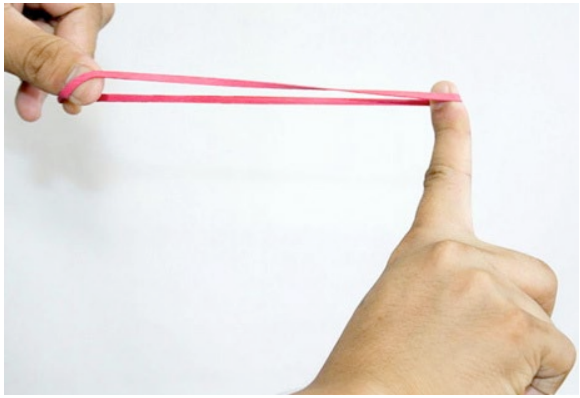
$$\sqrt{\langle r^2 \rangle} = N^{\nu} a \sqrt{\left(\frac{1 + cos\theta}{1 - cos\theta}\right)\left(\frac{1 - \langle cos\phi \rangle}{1 + \langle cos\phi \rangle}\right)}$$

Flow behavior/elastic properties

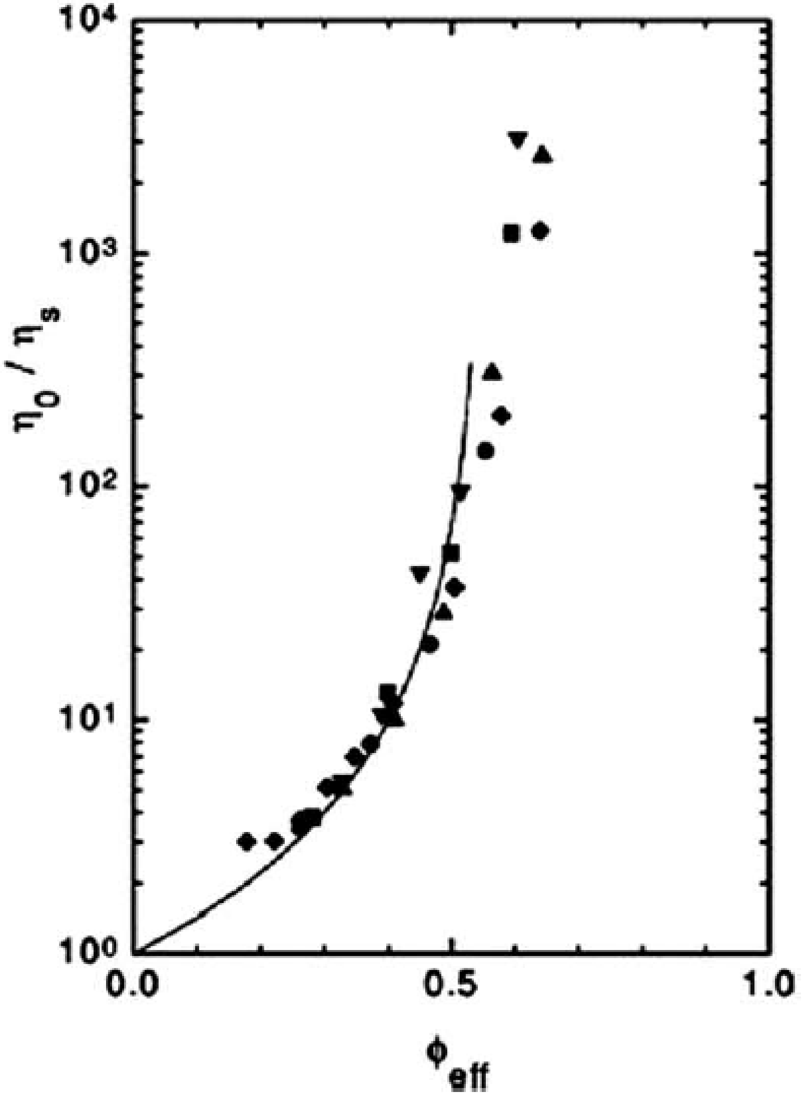
viscous

viscoelastic

elastic



Viscosity of polymer solutions

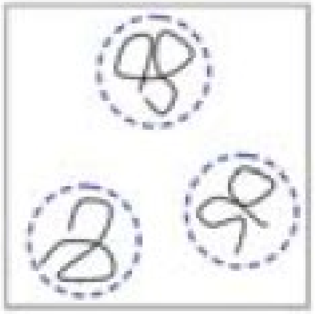


H. Senff and W. Richtering, *Journal of Chemical Physics*, 1999, **111**, 1705-1711

Polymer concentration

Do adjacent polymers interact with each other?

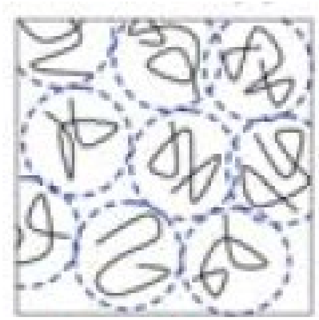
dilute



$c < c_m{}^*$

viscous

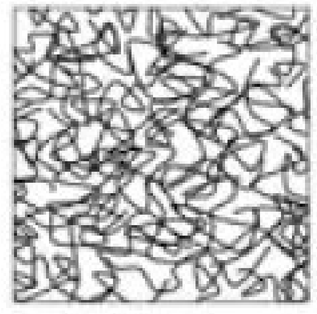
semi-dilute



$c = c_m{}^*$

viscoelastic

concentrated



$c > c_m{}^*$

elastic

$$c_m^* = \frac{N}{R_g^3}$$

$$c_m^* \propto N^{1-3\nu}$$

$c_m{}^*$: coil overlap concentration [molecules/m^3]
N: number of repeat units [-]
R_g: radius of gyration [m]
υ: Flory exponent [-]

Wang, Y. Z.; Li, B. H.; Xiong, X. M.; Wang, B.; Zhang, J. X. *Soft Matter* **2010,** *6* (14), 3318-3324

A polymer has a molar mass of 86 kg/mol and is composed of 1000 identical monomers, each 2 nm in length. What is the end-to-end distance?

A. 7.7 nm

B. 77 nm

C. 770 nm

D. 2000 nm

E. 5000 nm

$$\langle r^2 \rangle_0 = Na^2 \left(\frac{1 + cos\theta}{1 - cos\theta} \right)$$

$\Theta = 71°$

With this end-to-end distance and assuming the polymer behaves like an ideal chain, what is the concentration at which the solution enters the semi-dilute regime?

A. 4.1 μM

B. 4.1 mM

C. 41 mM

D. 410 mM

E. 4100 M

$$c_m^* := \frac{N}{R_g^3}$$

$N_A = 6.02\times10^{23}$ molecules/mol

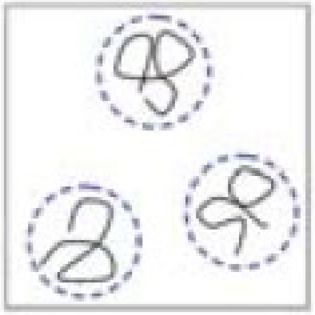
Polymer concentration

Do adjacent polymers interact with each other?

$$c_m^* := \frac{N}{R_g^3} \qquad c_m^* \propto N^{1-3\nu}$$

c_m^*: coil overlap concentration [molecules/m^3]
N: number of repeat units [-]
R_g: radius of gyration [m]
υ: Flory exponent [-]

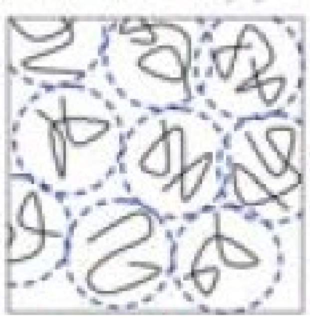
dilute



$c < c_m^*$

viscous

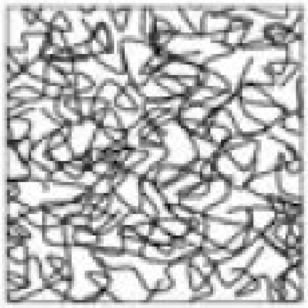
semi-dilute



$c = c_m^*$

viscoelastic

concentrated



$c > c_m^*$

elastic

Wang, Y. Z.; Li, B. H.; Xiong, X. M.; Wang, B.; Zhang, J. X. *Soft Matter* **2010,** *6* (14), 3318-3324

Viscosity of polymer solutions

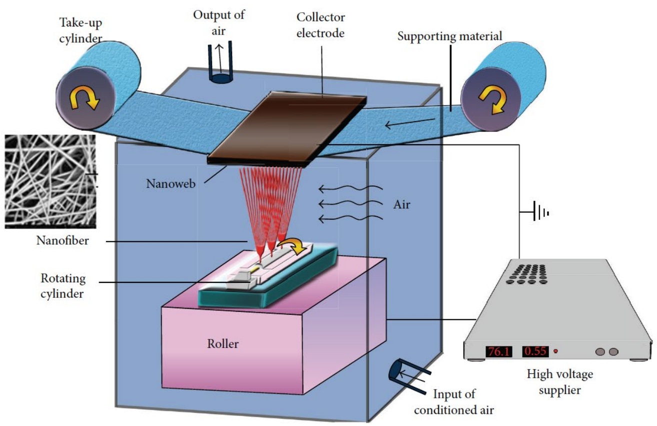
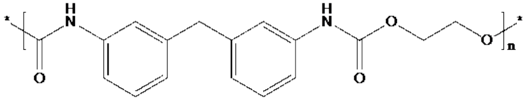
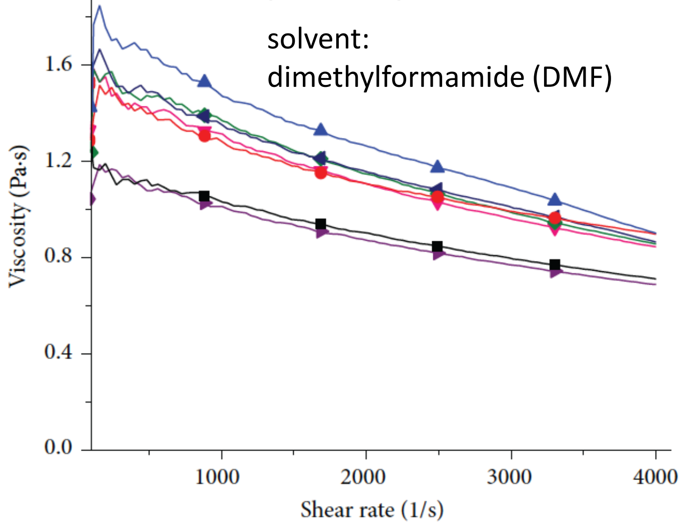


FIGURE 1: Diagram of the roller electrospinning system.

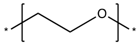
poly(urethane)

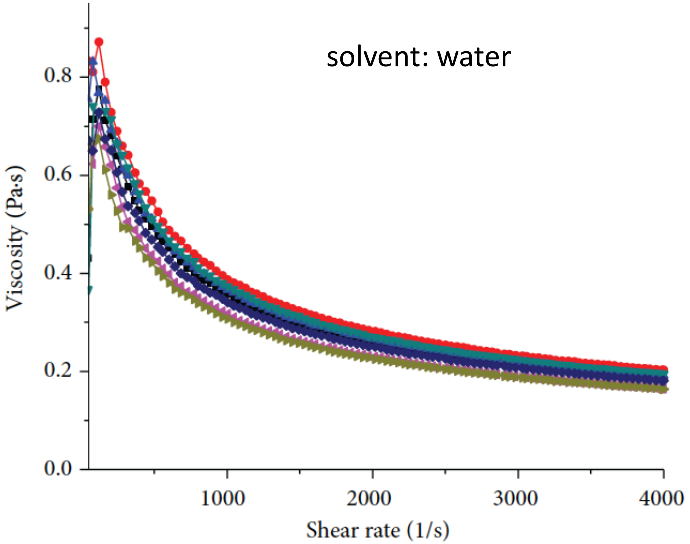




solvent:
dimethylformamide (DMF)

poly(ethylene oxide) (400 kDa)





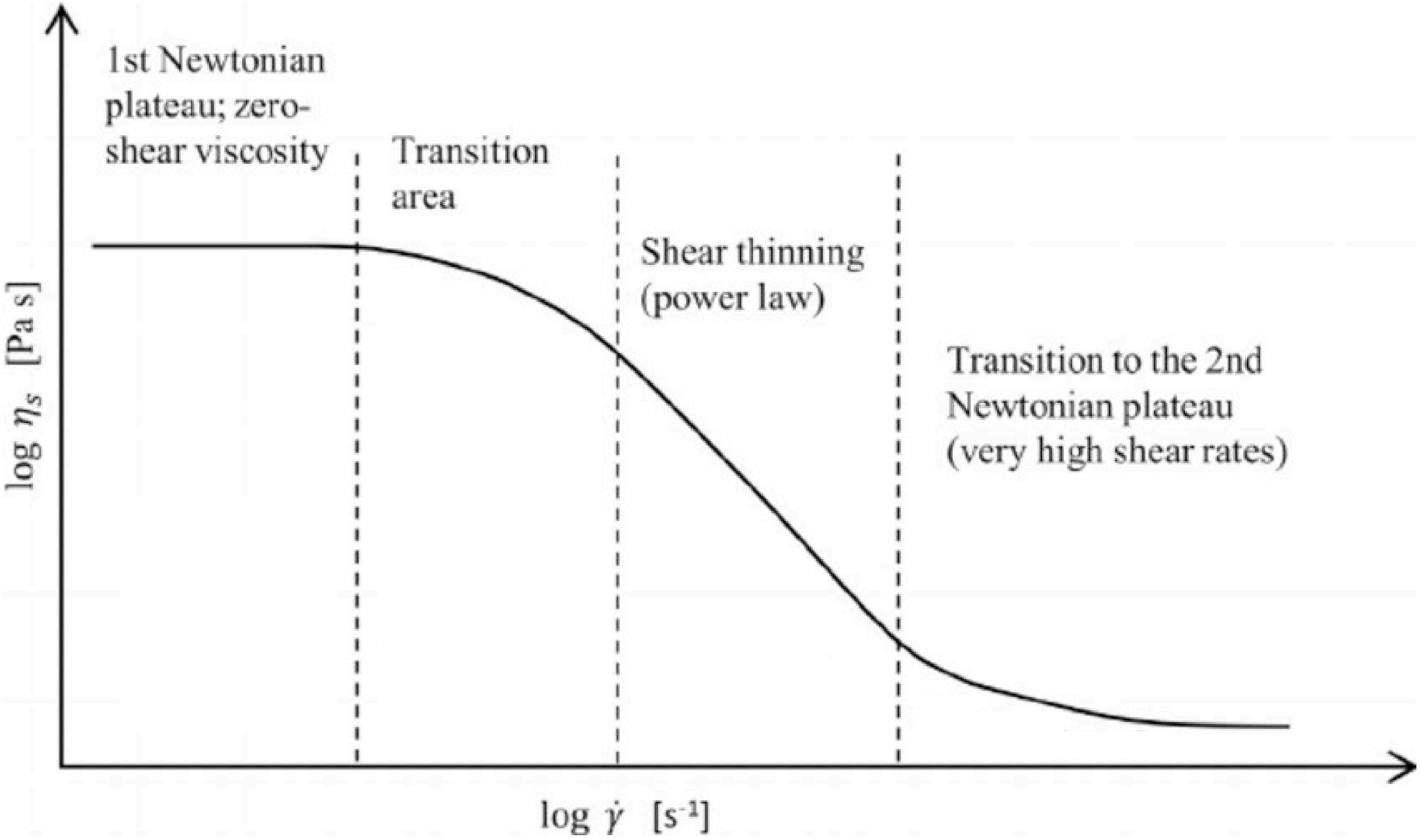
solvent: water

F. Yalcinkaya, B. Yalcinkaya and O. Jirsak, *Journal of Nanomaterials*, 2015

Outline

- Introduction
  - Isomerism
  - Tacticity
- Influence of polymer structure on crystallinity
- Dimensions of polymer chains
- Polymer solutions
- Polymer melts
- Polymers
  - Thermoplasts
  - Thermosets
  - Elastomers
- Recycling of polymers
- Characterization of polymers
- Application

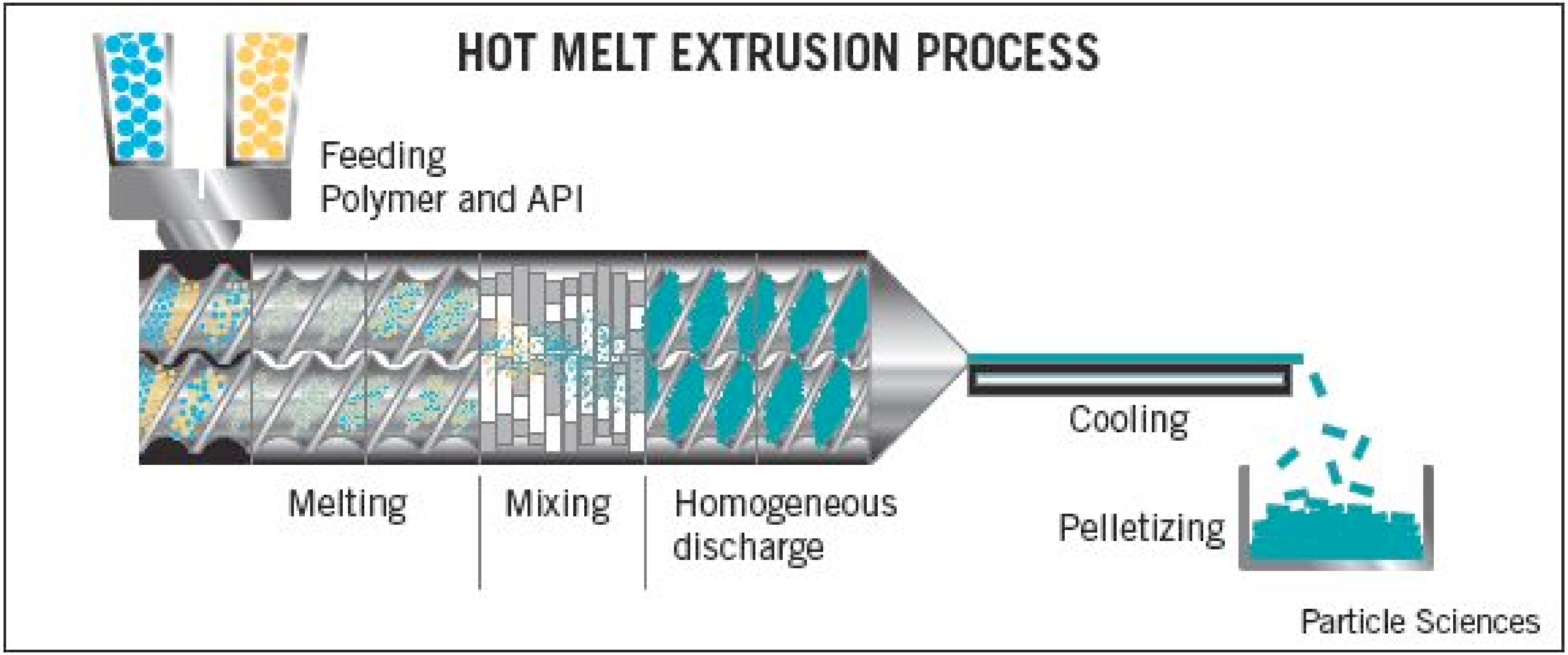
Flow behavior of polymer melts



J. Aho, J. P. Boetker, S. Baldursdottir and J. Rantanen, *Int. J. Pharm.*, 2015, **494**, 623-642

Polymer melts

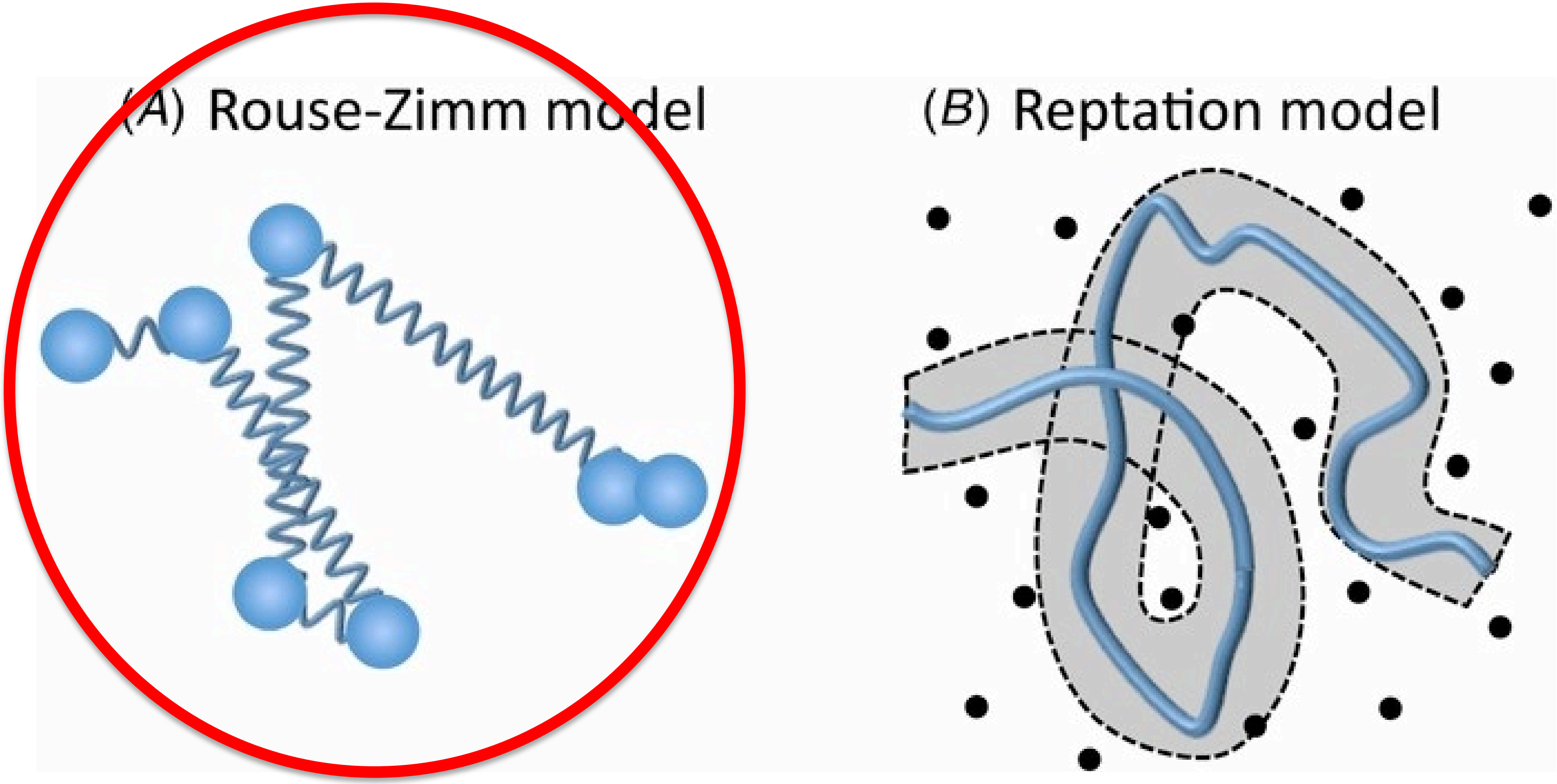
Figure 1



http://www.particlesciences.com/news/technical-briefs/2011/hot-melt-extrusion.html

Flow behavior of spaghetti

Flow of polymers in melts

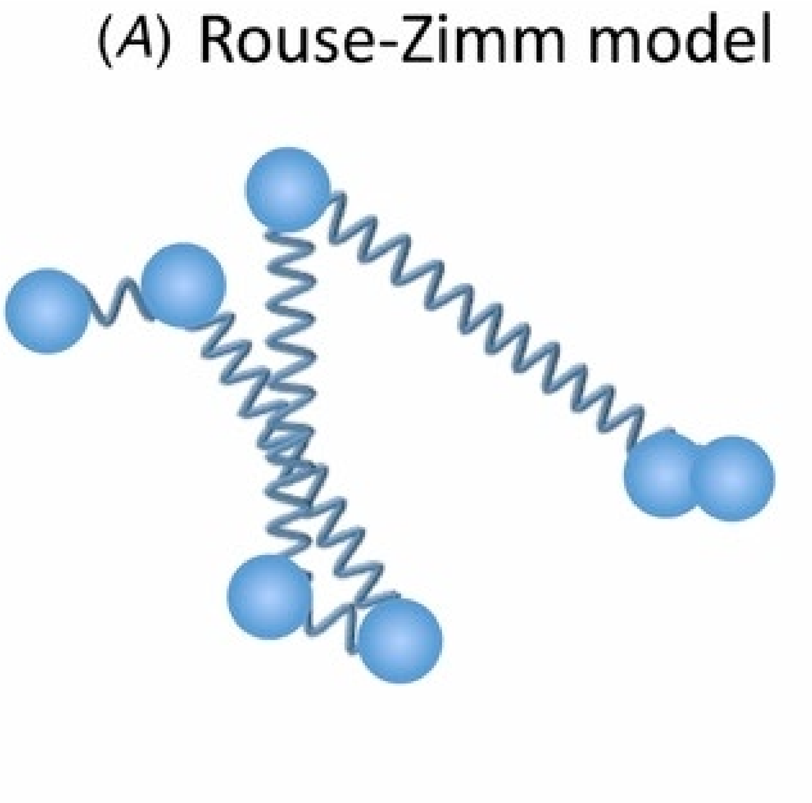


Flow of un-entangled polymers.

One chain moves through network of others.

Steven S Andrews, 2014, Phys. Biol. 11

Flow of polymers in melts

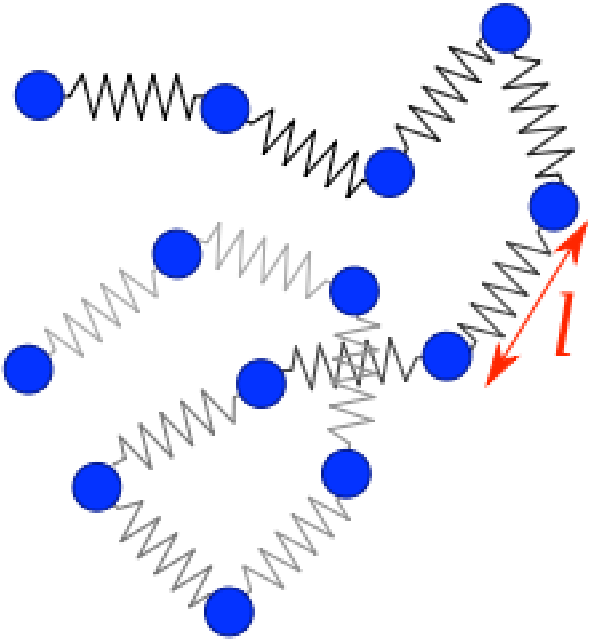


Flow of un-entangled polymers.

Steven S Andrews, 2014, Phys. Biol. 11

Rouse-Zimm Model

Description of conformational changes of an ideal chain.



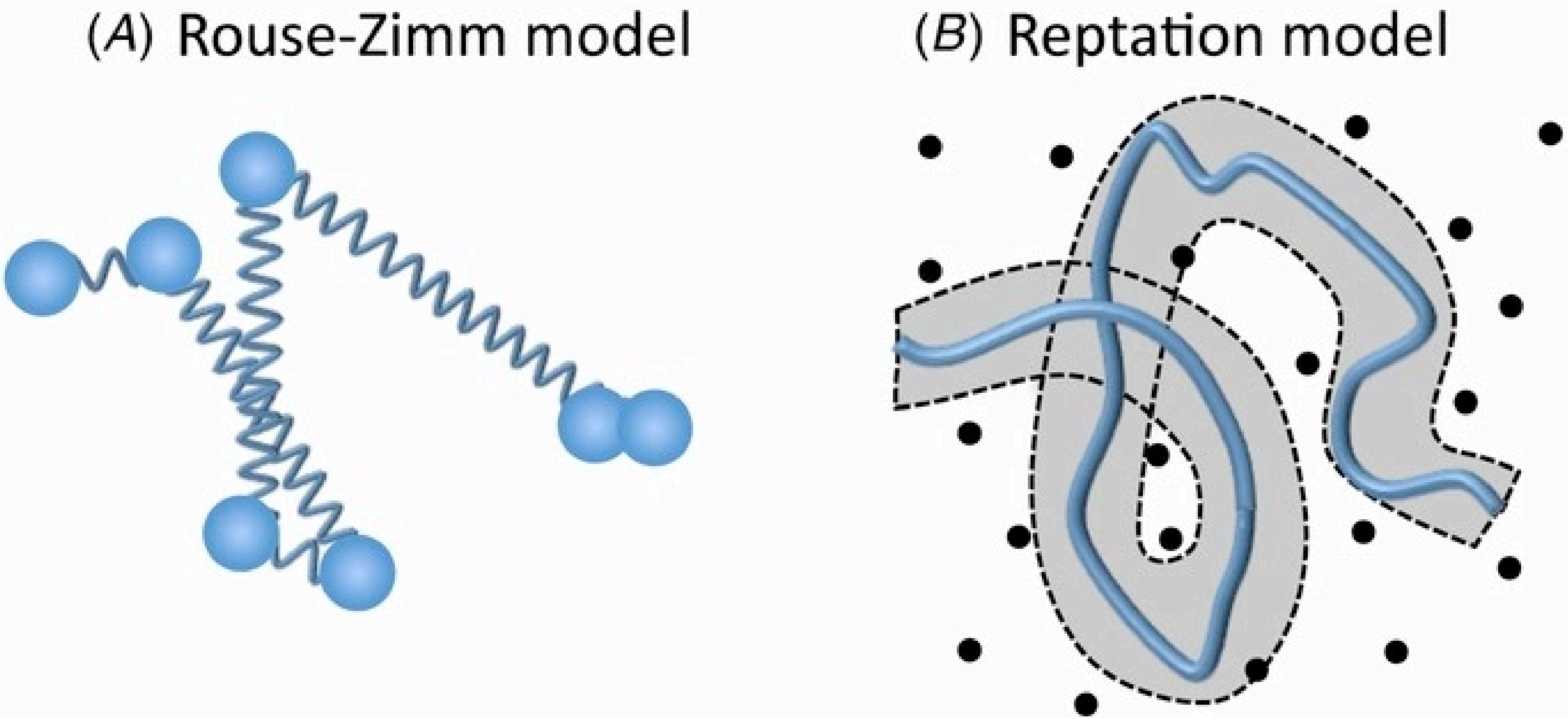
https://en.wikipedia.org/wiki/Rouse_model

- Segments are connected by springs
- Segment diffusion follows Brownian motion
- The diffusion coefficient scales with $D \propto \frac{1}{N^{\upsilon}}$

D: Diffusion coefficient [m^2/s]
N: Number of segments [-]
v: Flory exponent [-]

But: It is only a good model for polymers that are not entangled.

Flow of polymers in melts

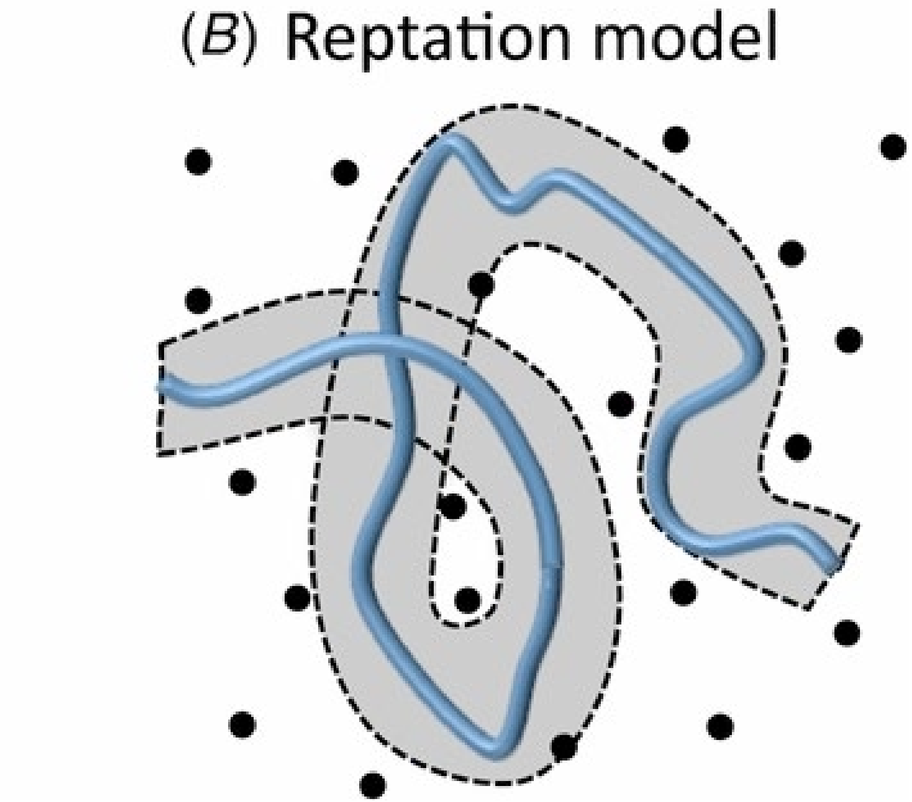


Flow of un-entangled polymers.

One chain moves through network of others.

Steven S Andrews, 2014, Phys. Biol. 11

Flow of polymers in melts



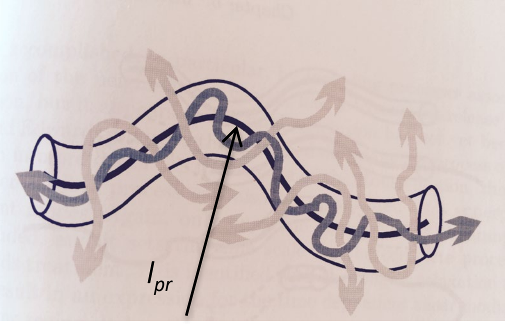
One chain moves through network of others.

Steven S Andrews, 2014, Phys. Biol. 11

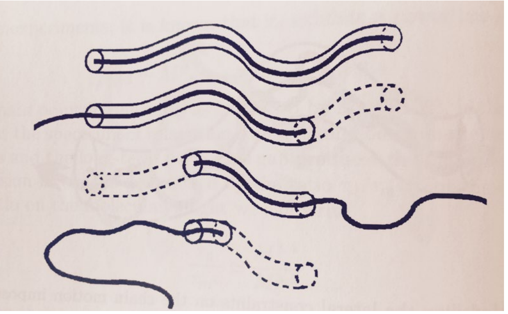
Reptation model

$$\langle r^2 \rangle = R_0^2 = N_R a_R^2 = l_{pr}\ a_{pr}$$

$$\widehat{D} = \frac{k_B T}{\zeta_p}$$



chain motion



G. Strobl, *The Physics of Polymers*.
(Springer-Verlag, Berlin Heidelberg, 1997)

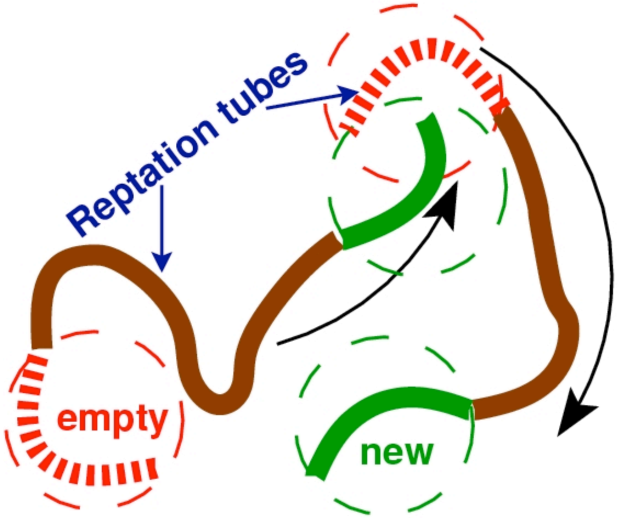
$\langle \boldsymbol{r}^2 \rangle$: average end-to-end distance [m^2]
l_{pr}: contour length of primitive path [m]
a_{pr}: associated sequence length of primitive path [m]
$\widehat{D}$: associated curvilinear diffusion coefficient [m^2/s]
ζ_p: friction coefficient of the chain [Ns/m]
τ_d: time required to disentangle [s]

Because there are no entanglements within the tube: $\zeta_P = N_R \zeta_R$ ➔ $\widehat{D} = \dfrac{k_B T}{N_R \zeta_R}$

The time required to lead to complete disentanglement: $\tau_d = \dfrac{l_{pr}^2}{\widehat{D}}$ ➔ $\tau_d \propto \zeta_R N_R^3$

Reptation

How does the polymer molecular weight influence the diffusion coefficient of polymers in melts?



http://www-ics.u-strasbg.fr/etsp//research/poly/high_snakedyn.php

$\langle r^2 \rangle$: average end-to-end distance [m^2]
l_{pr}: contour length of primitive path [m]
a_{pr}: associated sequence length of primitive path [m]
D: associated curvilinear diffusion coefficient [m^2/s]
ζ_R: friction coefficient of the chain [Ns/m]
τ_d: time required to disentangle [s]

For non-entangled polymer chains:

$$D = \frac{k_B T}{N_R^{\upsilon} \zeta_R} \propto \frac{1}{M_W^{\nu}}$$

For entangled polymer chains:

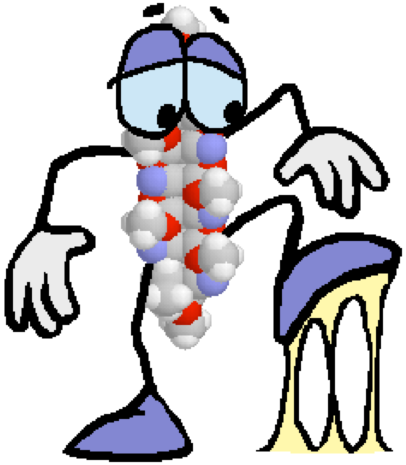
$$D = \frac{\langle r^2 \rangle}{6 \Delta t}$$

$$D \propto \frac{l_{pr} a_{pr}}{\tau_d} \propto \frac{N_R}{N_R^3} \propto \frac{1}{M_W^2}$$

In which case does the viscosity increase most strongly if the molecular weight of the polymer/monomer is increased?

A. of non-entangled polymers
B. For melts composed of entangled polymers
C. For melts composed of monomers

Viscosity of polymer melts



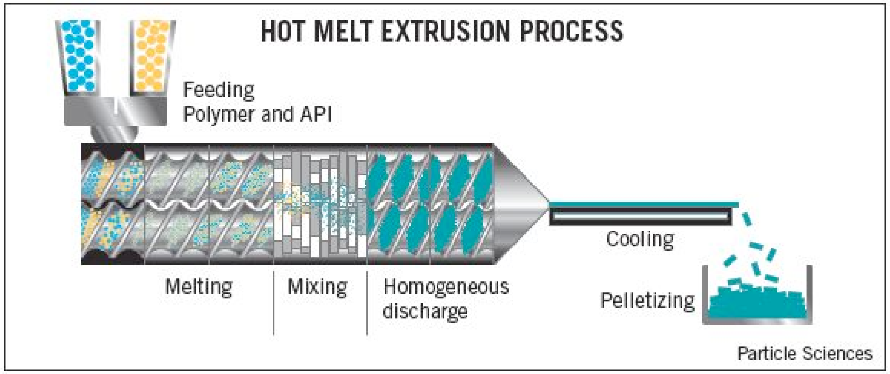
low M_w, no entanglements:

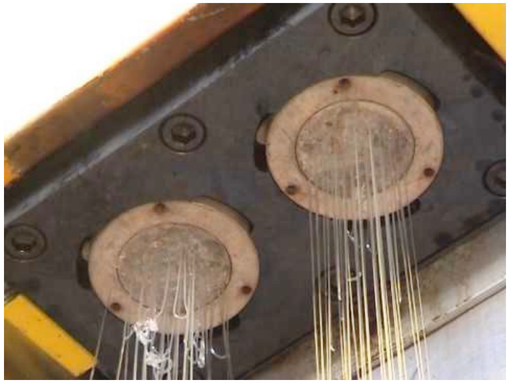
$$\eta_0 \propto M_w$$

high M_w, entanglements:

$$\eta_0 \propto M_w^{3.4}$$

Why does the viscosity of polymer melts matter?





http://www.particlesciences.com/news/technical-briefs/2011/hot-melt-extrusion.html

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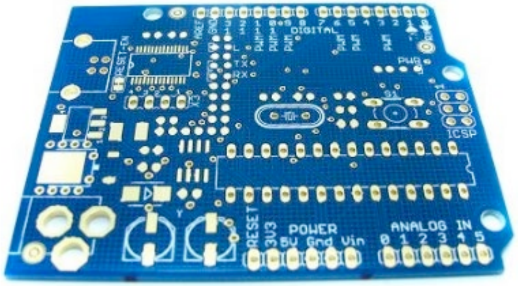
Polymers

Thermoplasts

Can be molten and when cooled form an amorphous or glassy structure

Thermosets

Harden when the temperature is increased ➔ crosslinking

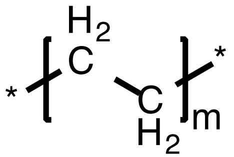


Elastomer

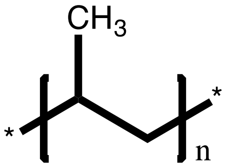
Can be stretched to many times their original dimension and recover if stress is released

Thermoplasts

Examples:



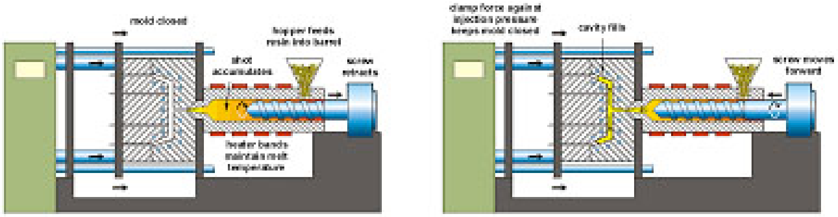
poly(ethylene)



poly(propylene)

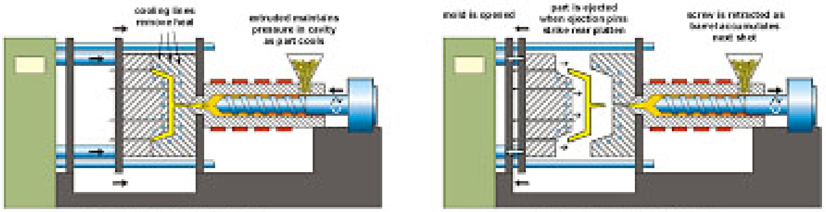
Analogy:

Processing:



(a) – step 2: plasticizing

(b) – step 3: injecting



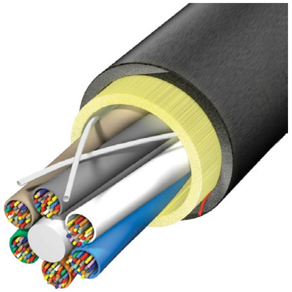
(c) – step 3: cooling

(d) – step 4: ejecting

http://www.idsa-mp.org/proc/plastic/injection/injection_process.htm

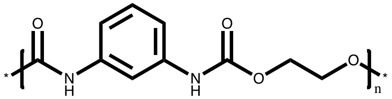
Polymers contained in thermoplasts are physically crosslinked, they are entangled.

Any change caused by heating is reversible, as long as the temperature is kept below the thermal decomposition temperature.

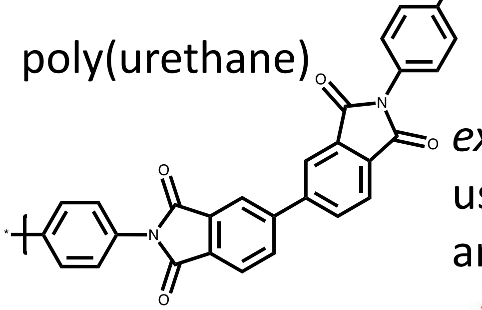


Thermosets

Examples:



poly(urethane)



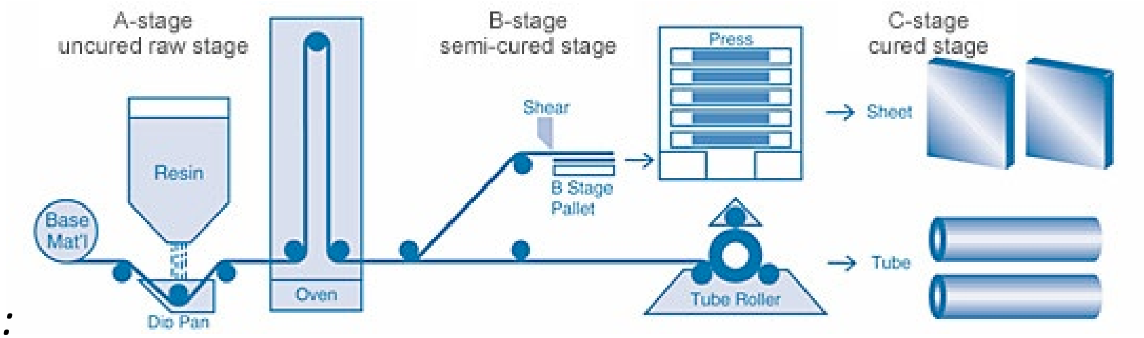
poly(imide)

Analogies:

Processing:

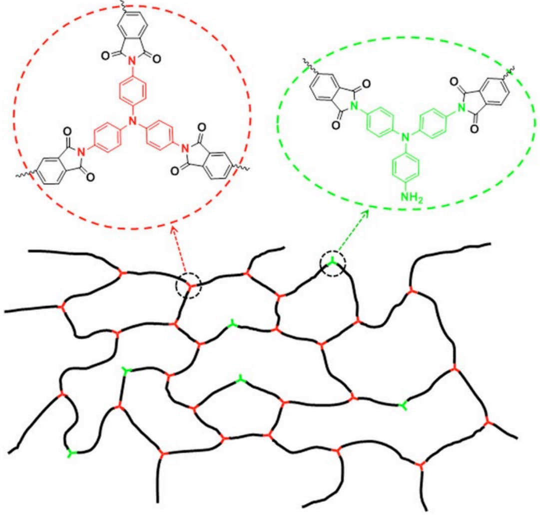
1. mix components

2. cure



http://www.acculam.com/processes.html

example:
use of tris(4-aminophenyl) amine as crosslinker



X. Xiao, D. Kong, X. Qiu, W. Zhang, Y. Liu, S. Zhang, F. Zhang, Y. Hu and J. Leng, *Scientific Reports*, 2015, **5**, 14137

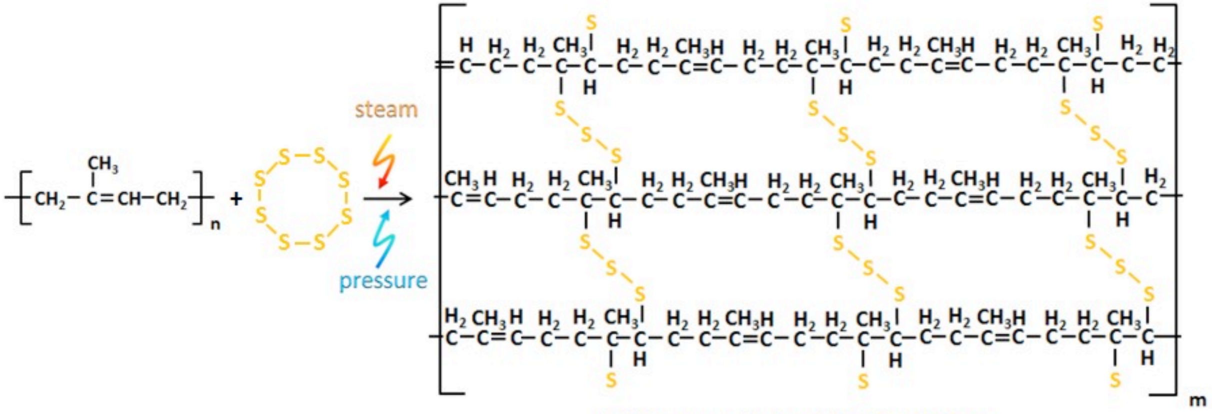
Polymers contained in thermosets are covalently crosslinked.

Elastomers

Processing:

Elastomers are formed by crosslinking linear chains.
If disulfide bonds are used to crosslink linear chains, this process is called vulcanization.

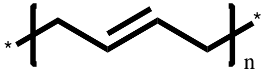
Vulcanization of Natural rubber (Polyisoprene)



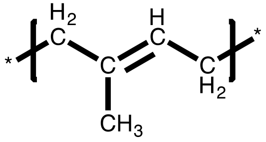
Polyisoprene chains with Sulfur Bridges

http://scinote.tumblr.com/

Examples:



poly(butadiene)



synthetic poly(isoprene)

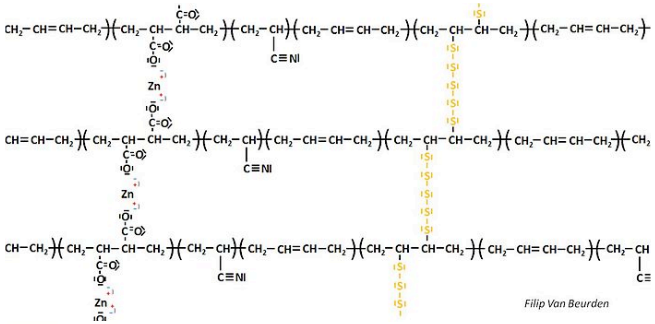
Analogy:

Elastomers are usually covalently crosslinked.

Elastomers have a low crosslink density, which makes them flexible.

Elastomers

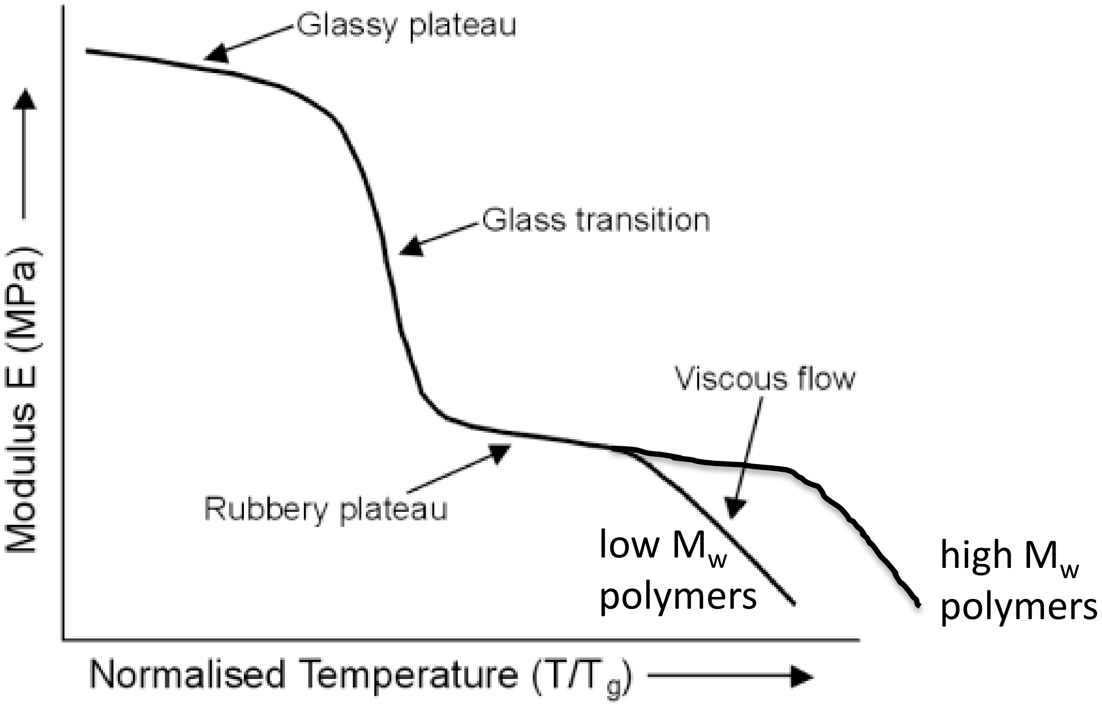
nitrile rubber



Filip Van Beurden

$T_g \approx -15\ °C - 30°C$

Elastic properties of polymers



At T_g:
The change in the polymer conformation is small.
The change in the chain mobility is large.

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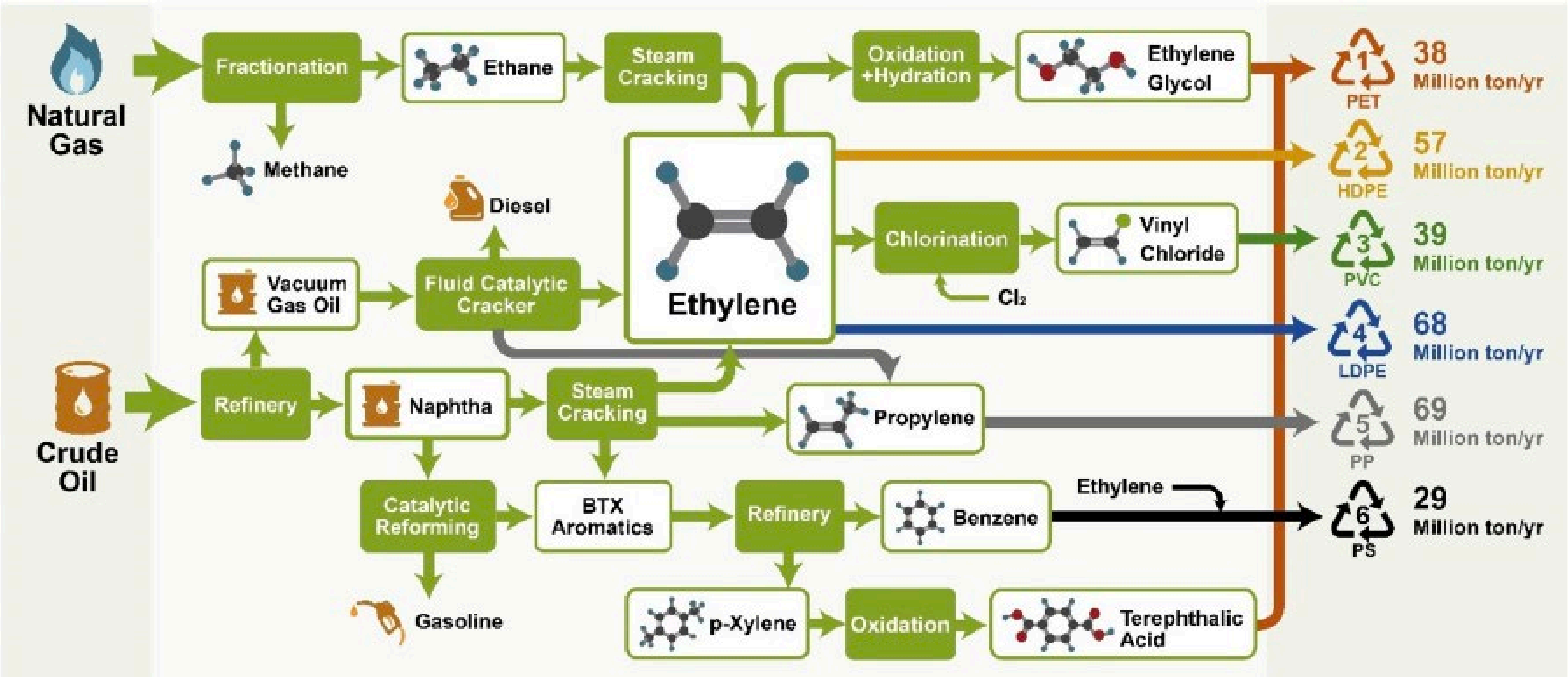
  - Thermosets
  - Elastomers
- Recycling of polymers
- Characterization of polymers
- Application

Plastic production

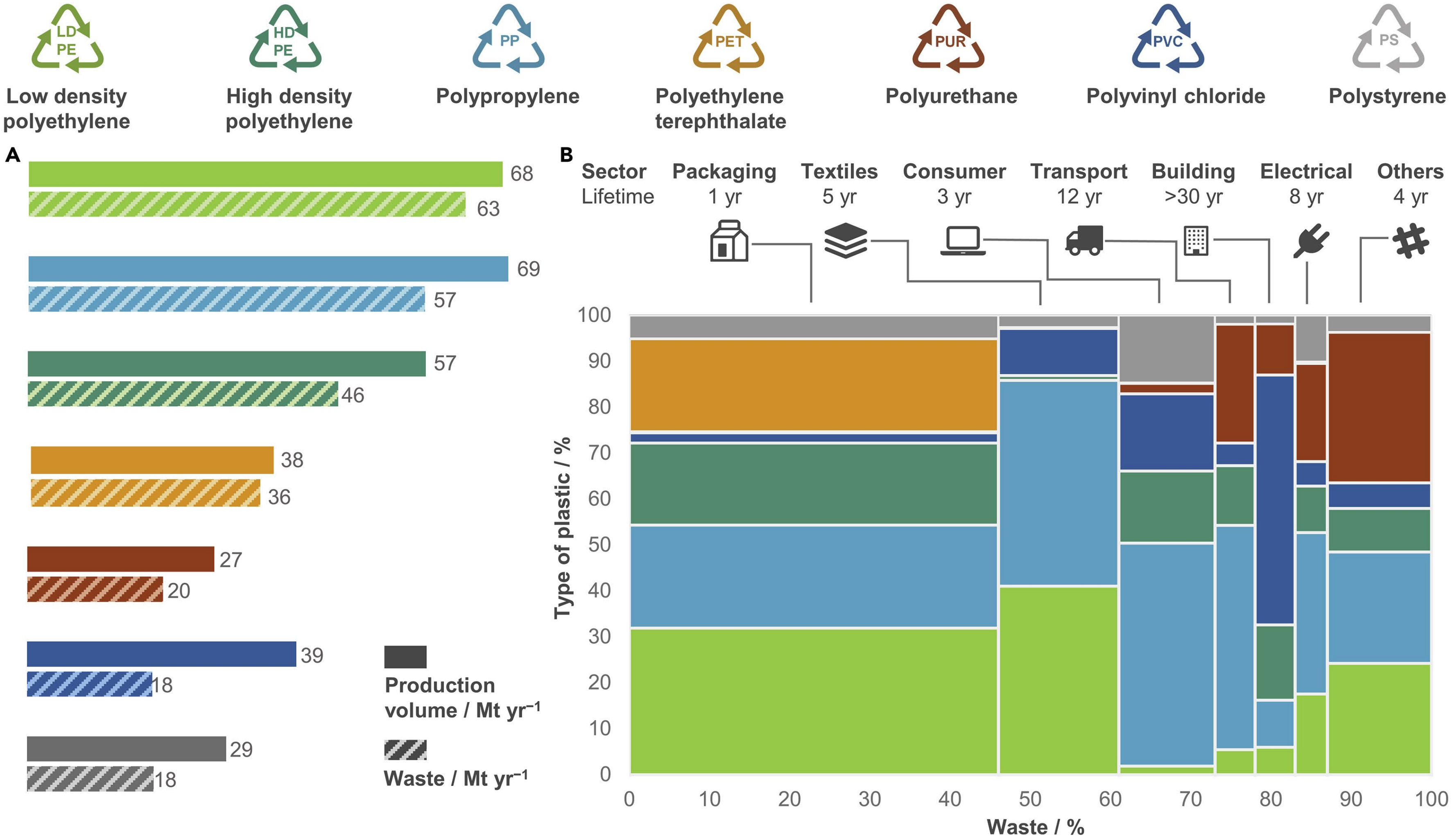


Natural Gas
Fractionation
Ethane
Steam Cracking
Methane
Crude Oil
Refinery
Vacuum Gas Oil
Fluid Catalytic Cracker
Diesel
Naphtha
Steam Cracking
Catalytic Reforming
Gasoline
BTX Aromatics
Refinery
Benzene
p-Xylene
Oxidation
Terephthalic Acid
Ethylene
Oxidation +Hydration
Ethylene Glycol
Chlorination
Cl_2
Vinyl Chloride
Propylene
Ethylene

1 PET – 38 Million ton/yr
2 HDPE – 57 Million ton/yr
3 PVC – 39 Million ton/yr
4 LDPE – 68 Million ton/yr
5 PP – 69 Million ton/yr
6 PS – 29 Million ton/yr

Martín, A.J., Mondelli, C., Jaydev, S.D., and Pérez-Ramírez, J. (2021). Catalytic processing of plastic waste on the rise. Chem 7, 1487–1533. https://doi.org/10.1016/j.chempr.2020.12.006

Plastic types

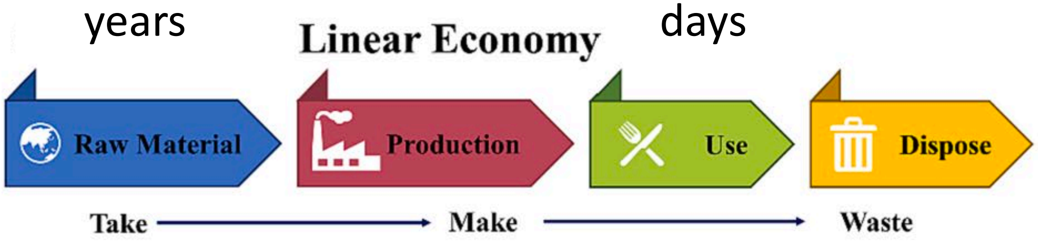


Martín, A.J., Mondelli, C., Jaydev, S.D., and Pérez-Ramírez, J. (2021). Catalytic processing of plastic waste on the rise. Chem *7*, 1487–1533. https://doi.org/10.1016/j.chempr.2020.12.006

What is the problem with plastics?

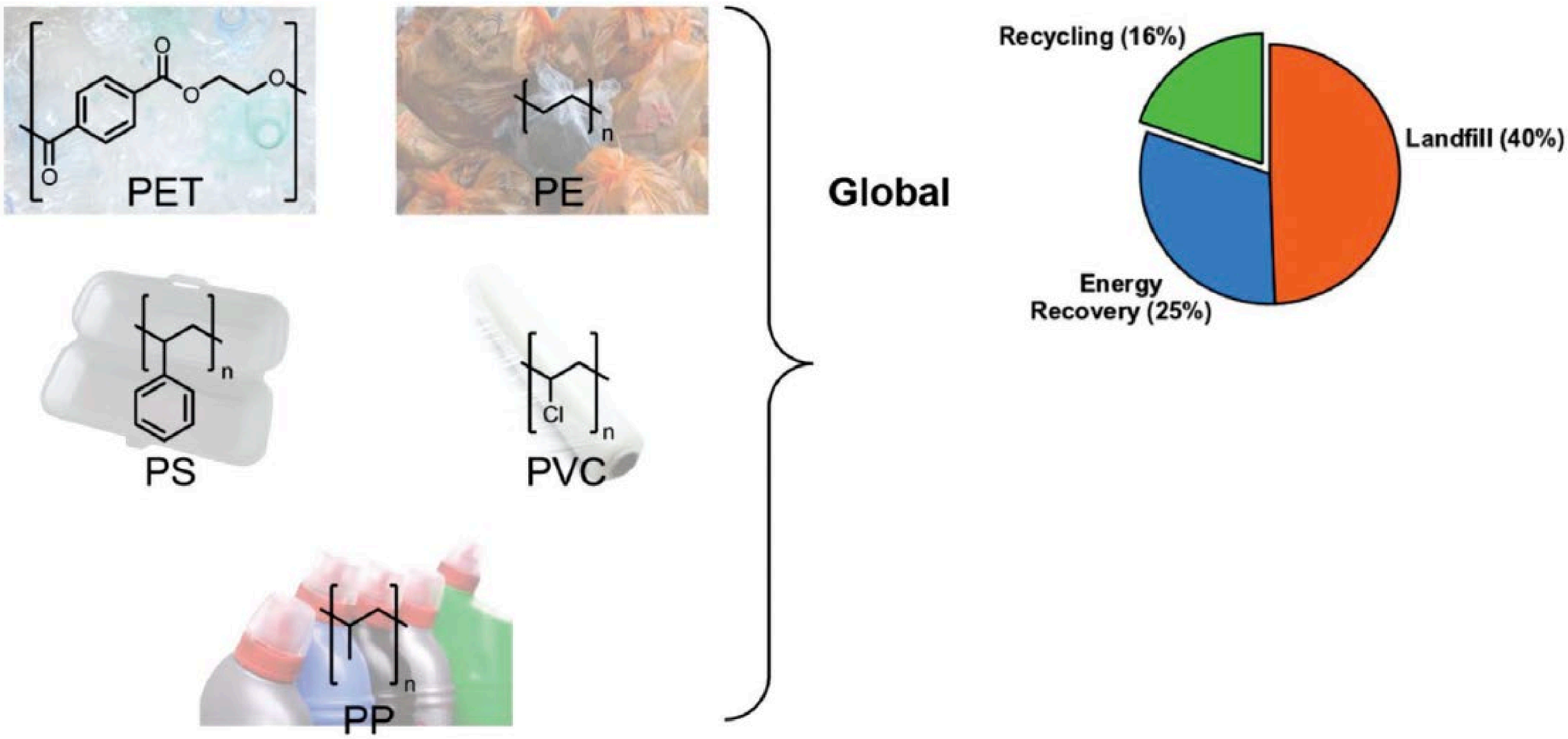
years

days



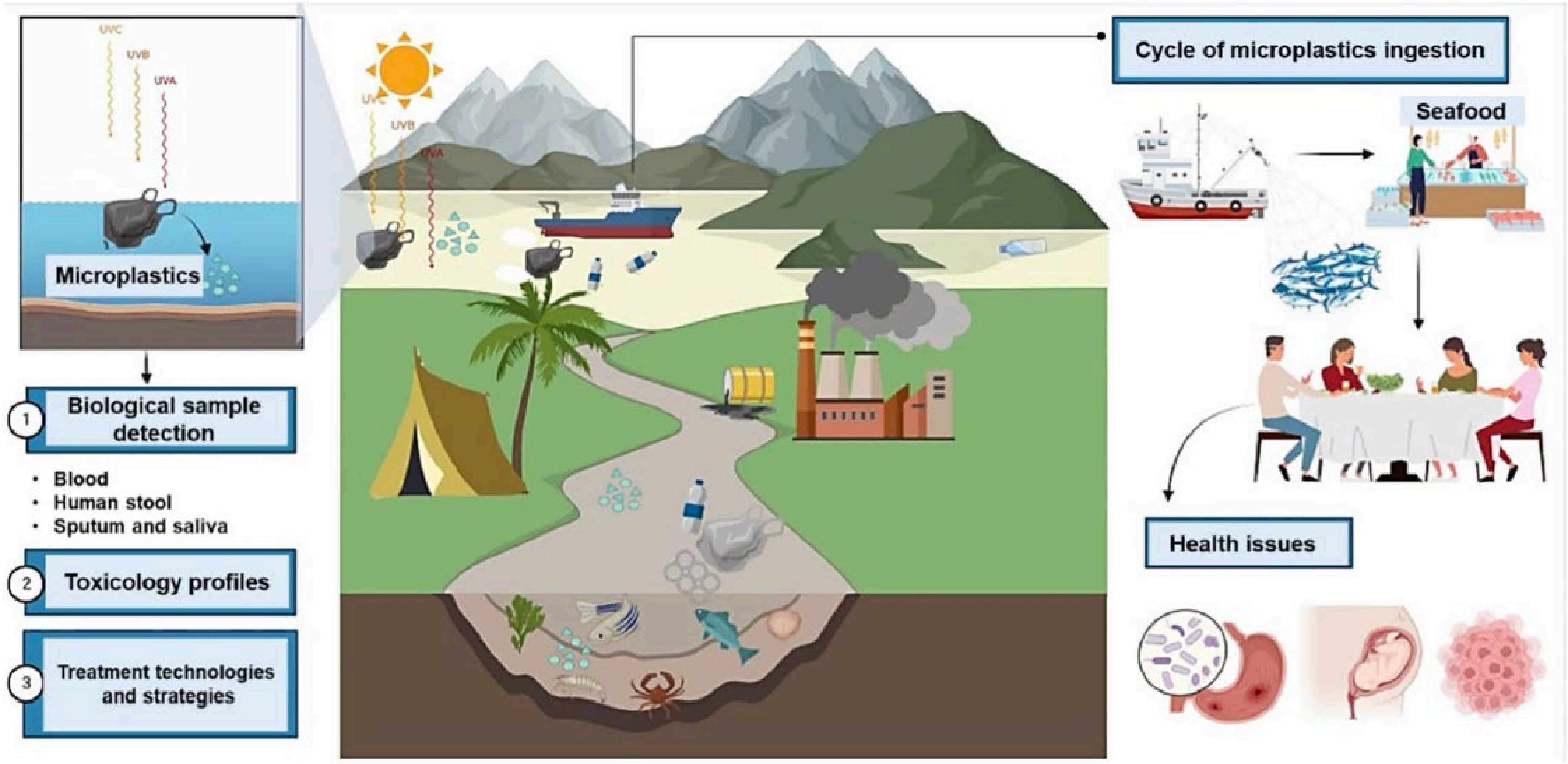
Hassan, M., Mohanty, A.K., and Misra, M. (2024). Materials & Design *237*, 112558. 10.1016/j.matdes.2023.112558

Recycling of polymers



Mechanical Recycling of Packaging Plastics: A Review - Schyns - 2021 - Macromolecular Rapid Communications - Wiley Online Library
https://onlinelibrary.wiley.com/doi/full/10.1002/marc.202000415

Problematic of landfill



1 Biological sample detection

- Blood
- Human stool
- Sputum and saliva

2 Toxicology profiles

3 Treatment technologies and strategies

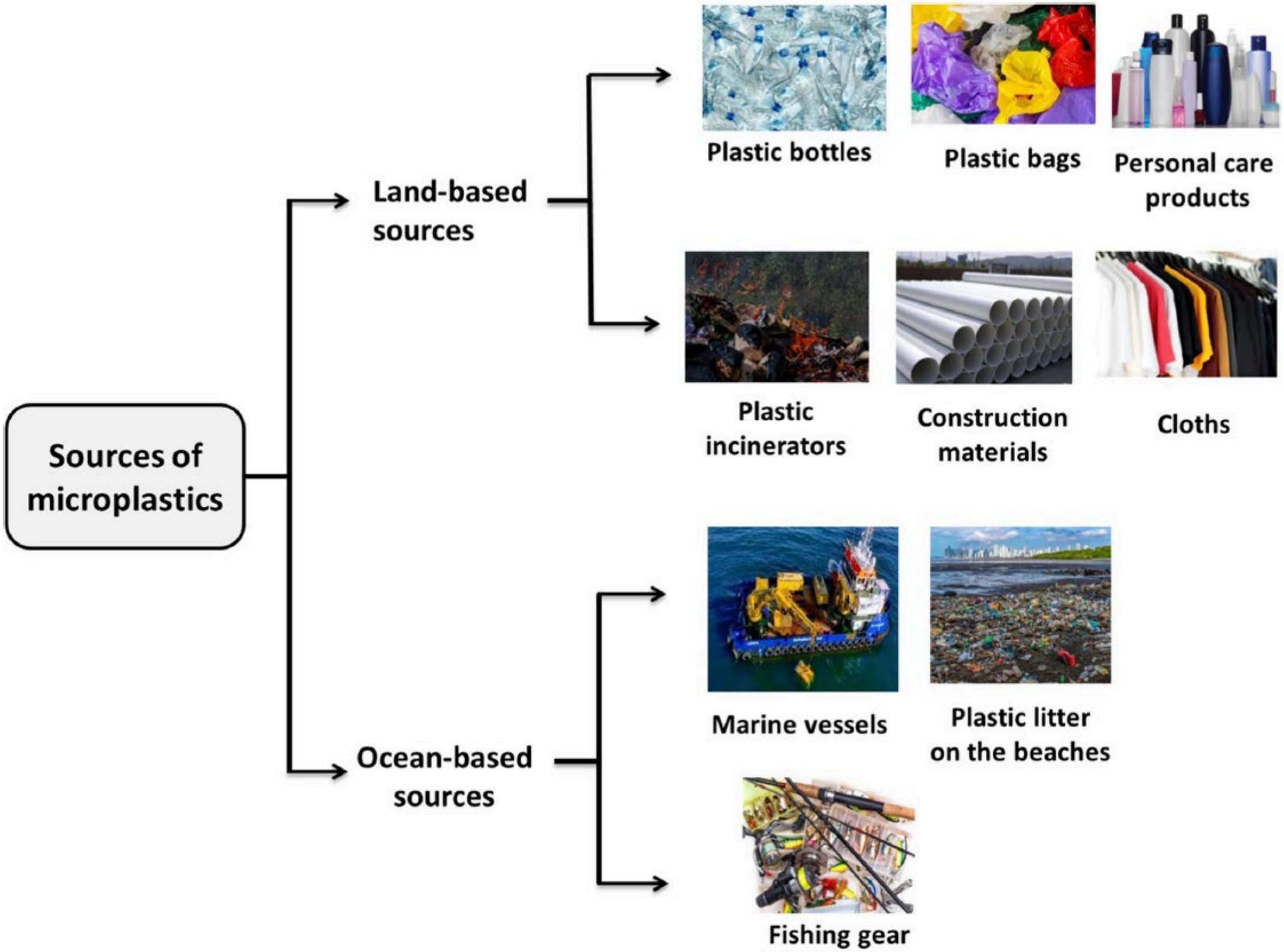
Cycle of microplastics ingestion

Seafood

Health issues

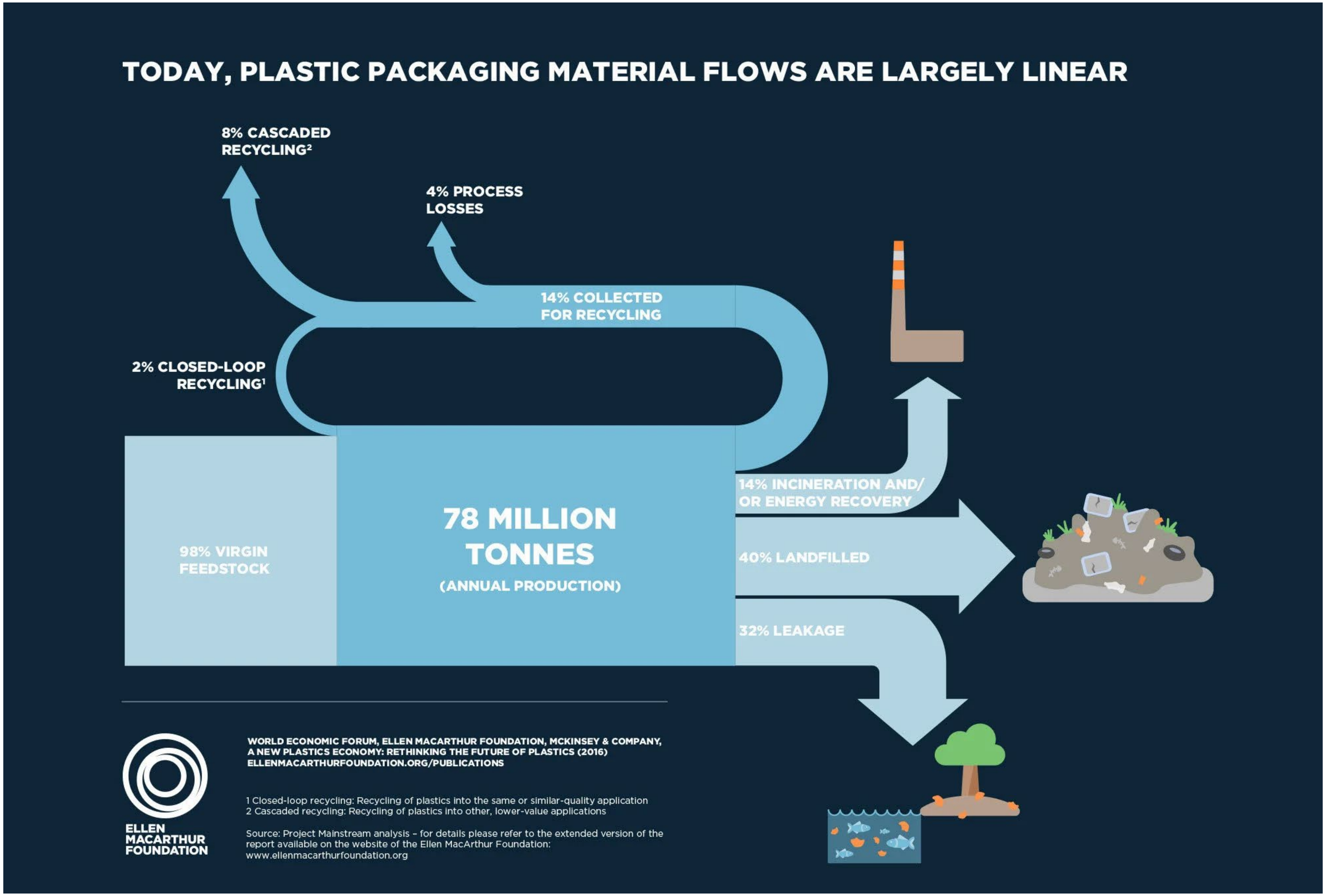
Osman, A.I., et al. (2023).. Environ Chem Lett *21*, 2129–2169. https://doi.org/10.1007/s10311-023-01593-3

Sources of microplastics



Osman, A.I., et al. (2023).. Environ Chem Lett *21*, 2129–2169. https://doi.org/10.1007/s10311-023-01593-3

Recycling of plastic packaging



TODAY, PLASTIC PACKAGING MATERIAL FLOWS ARE LARGELY LINEAR

8% CASCADED RECYCLING[2]

4% PROCESS LOSSES

14% COLLECTED FOR RECYCLING

2% CLOSED-LOOP RECYCLING[1]

98% VIRGIN FEEDSTOCK

78 MILLION TONNES

(ANNUAL PRODUCTION)

14% INCINERATION AND/ OR ENERGY RECOVERY

40% LANDFILLED

32% LEAKAGE

ELLEN MACARTHUR FOUNDATION

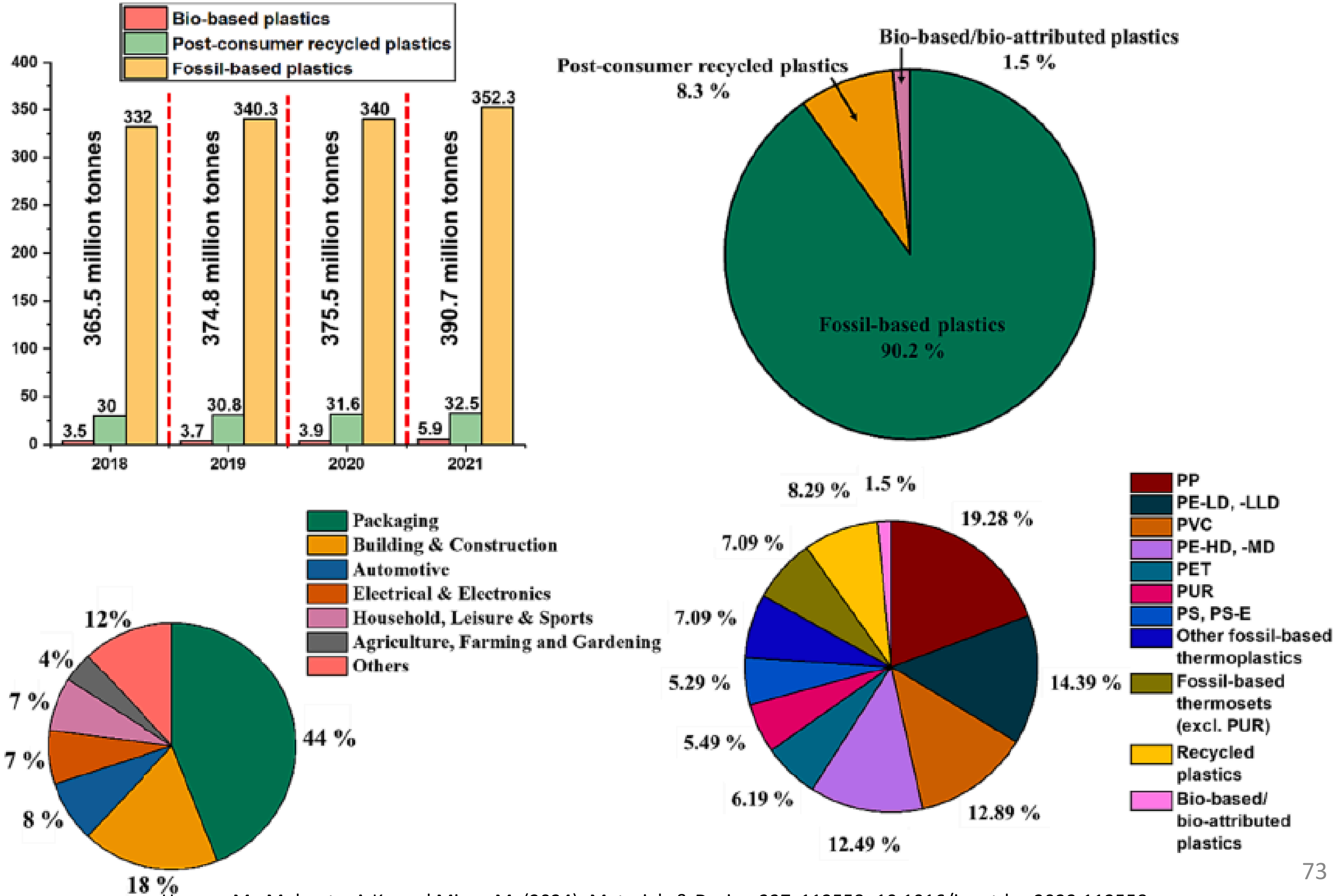
WORLD ECONOMIC FORUM, ELLEN MACARTHUR FOUNDATION, MCKINSEY & COMPANY,
A NEW PLASTICS ECONOMY: RETHINKING THE FUTURE OF PLASTICS (2016)
ELLENMACARTHURFOUNDATION.ORG/PUBLICATIONS

1 Closed-loop recycling: Recycling of plastics into the same or similar-quality application
2 Cascaded recycling: Recycling of plastics into other, lower-value applications

Source: Project Mainstream analysis – for details please refer to the extended version of the report available on the website of the Ellen MacArthur Foundation: www.ellenmacarthurfoundation.org

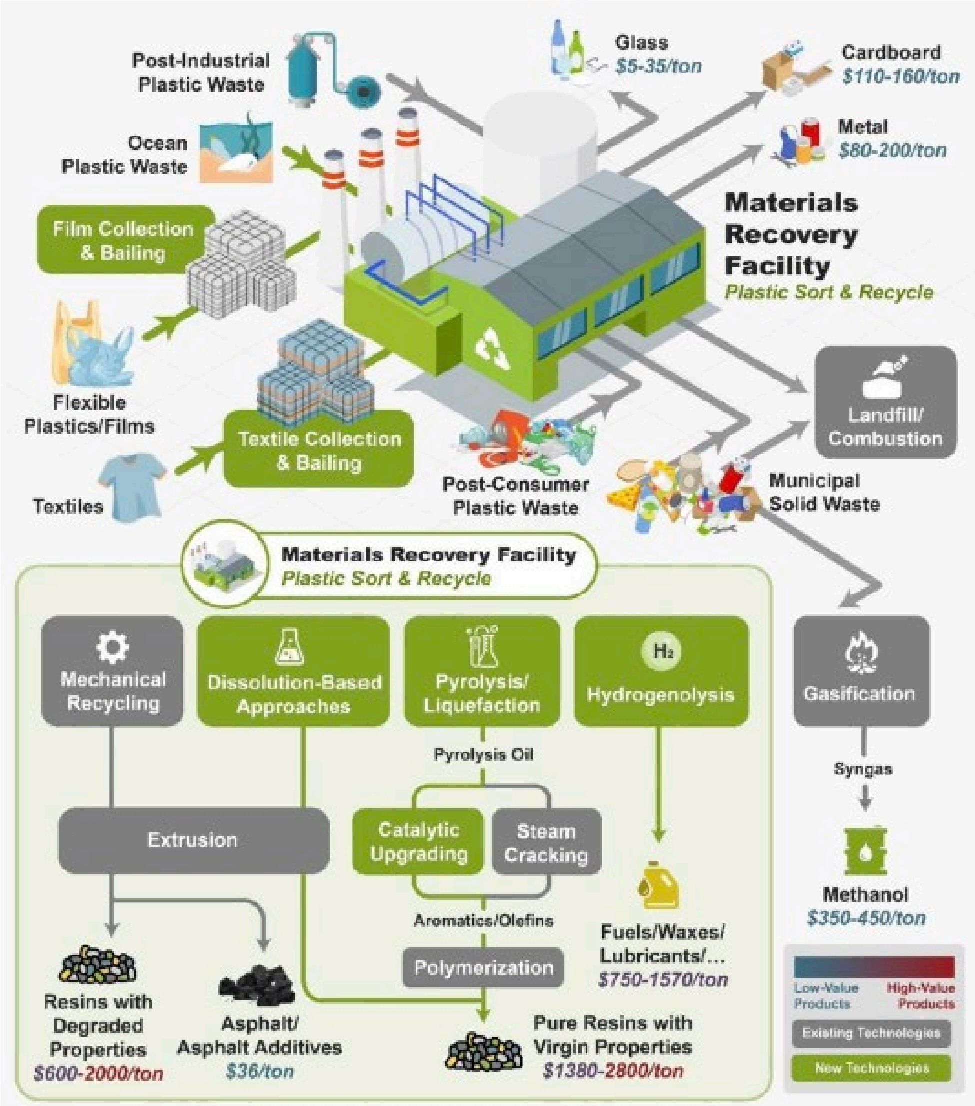
Plastics and the circular economy https://www.ellenmacarthurfoundation.org/plastics-and-the-circular-economy-deep-dive.

Recycling of polymers



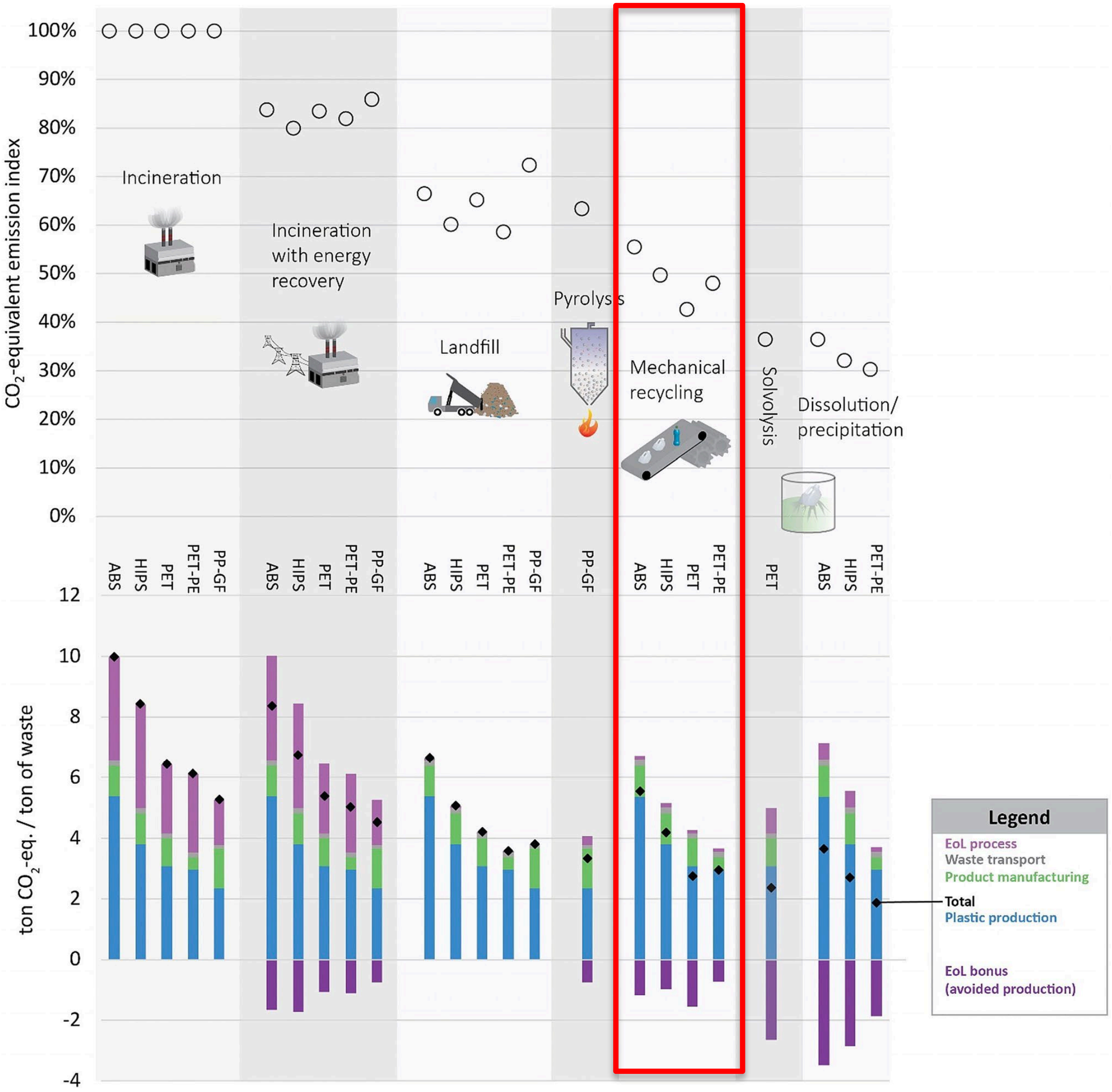
Hassan, M., Mohanty, A.K., and Misra, M. (2024). Materials & Design *237*, 112558. 10.1016/j.matdes.2023.112558

Recycling routes



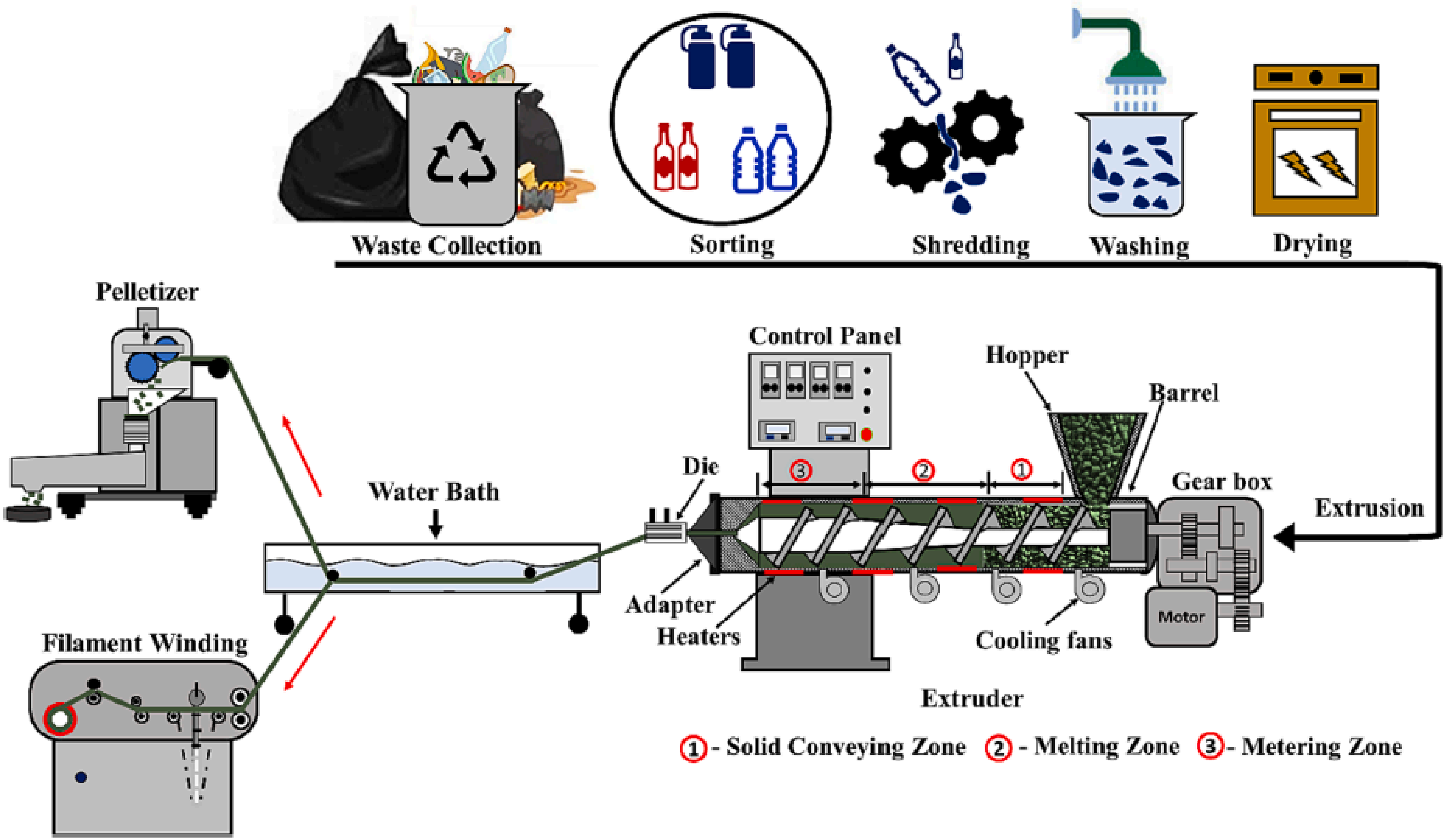
Li, H.,, et al. (2022). Green Chem. *24*, 8899–9002. https://doi.org/10.1039/D2GC02588D.

Different recycling routes



Mechanical Recycling of Packaging Plastics: A Review - Schyns - 2021 - Macromolecular Rapid Communications - Wiley Online Library
https://onlinelibrary.wiley.com/doi/full/10.1002/marc.202000415

Mechanical recycling

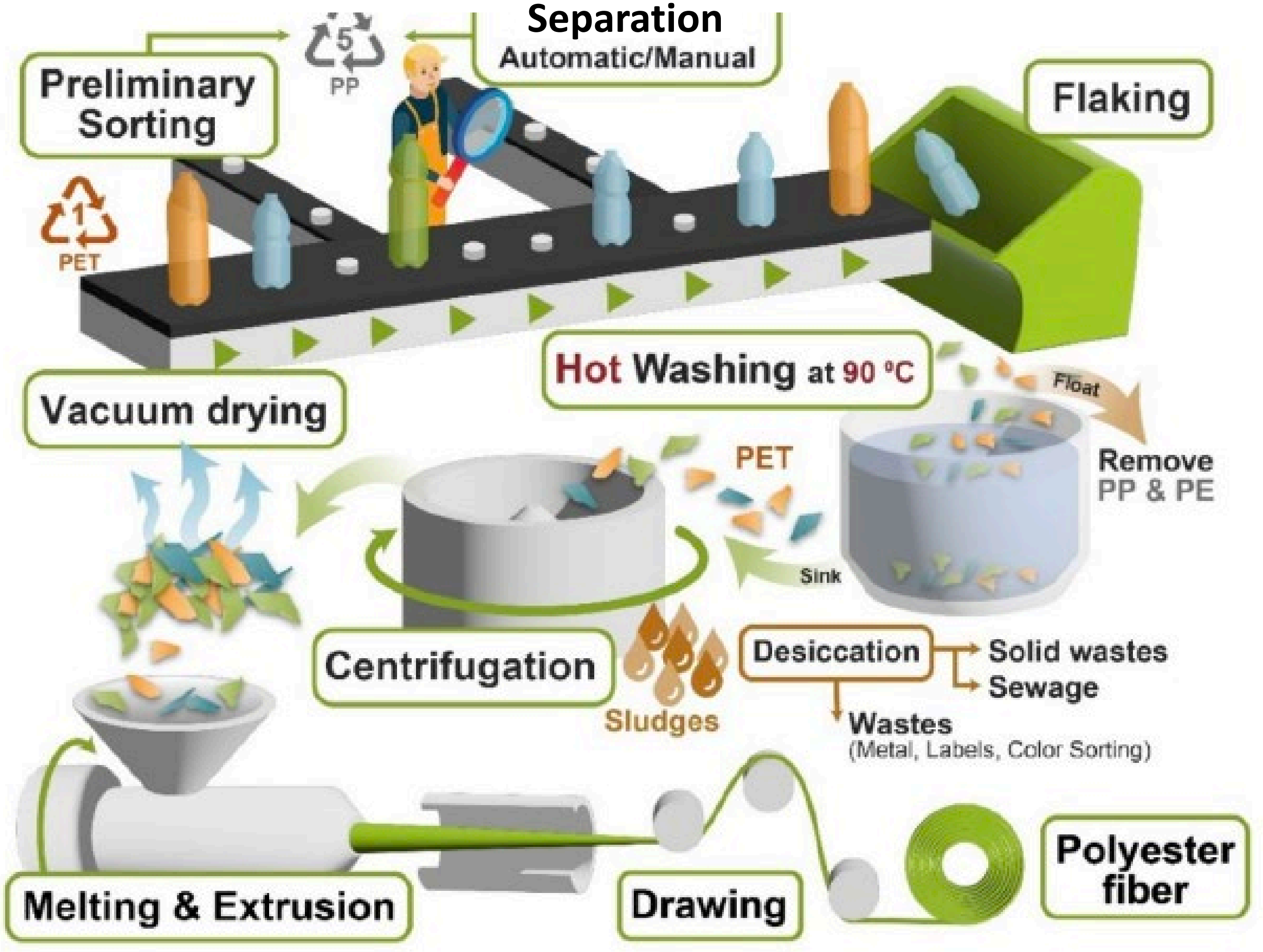


Hassan, M., Mohanty, A.K., and Misra, M. (2024). Materials & Design *237*, 112558. 10.1016/j.matdes.2023.112558

Mechanical recycling

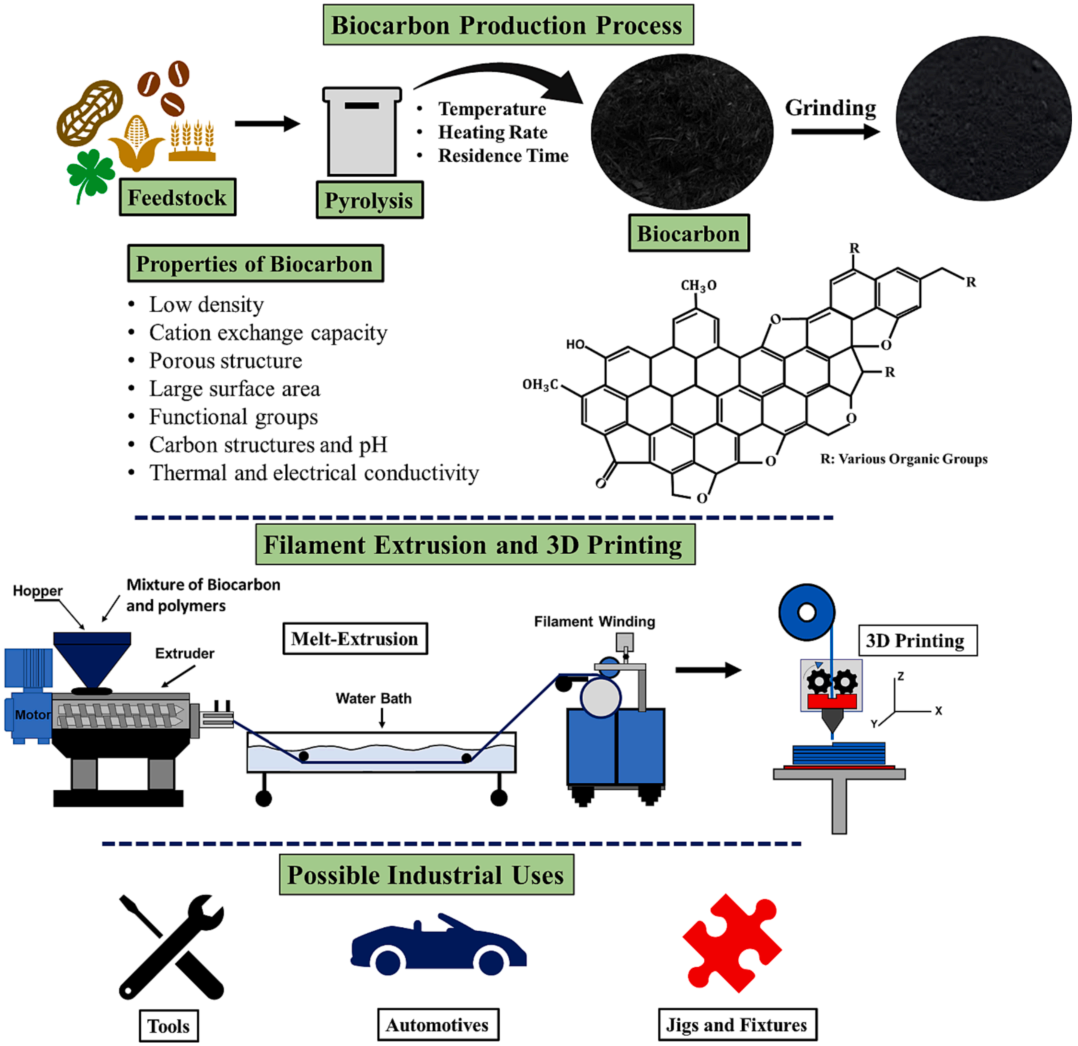
Soto, J.M., Blázquez, G., Calero, M., Quesada, L., Godoy, V., and Martín-Lara, M.Á. (2018). Journal of Cleaner Production *203*, 777–787. https://doi.org/10.1016/j.jclepro.2018.08.302

Mechanical recycling



Jabłońska, B., Kiełbasa, P., Korenko, M., and Dróżdż, T. (2019).. Energies *12*, 2197. https://doi.org/10.3390/en12112197

Transforming waste biomass into functional polymers



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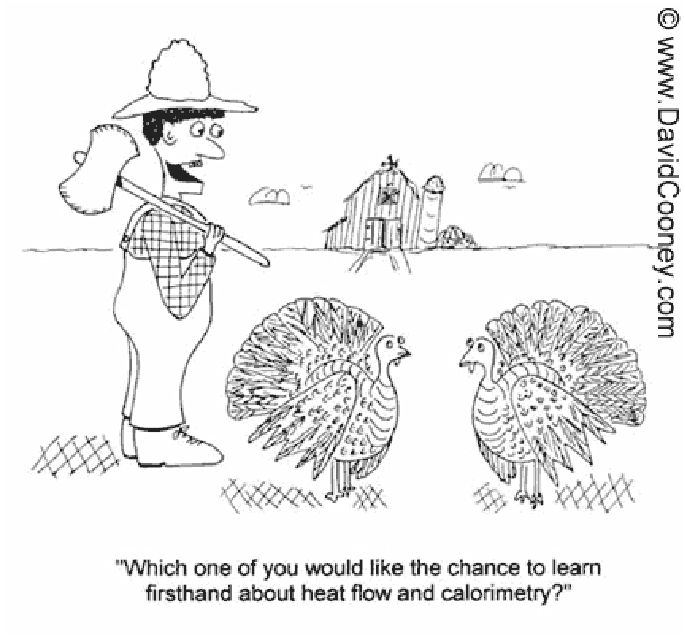
Characterization of polymers

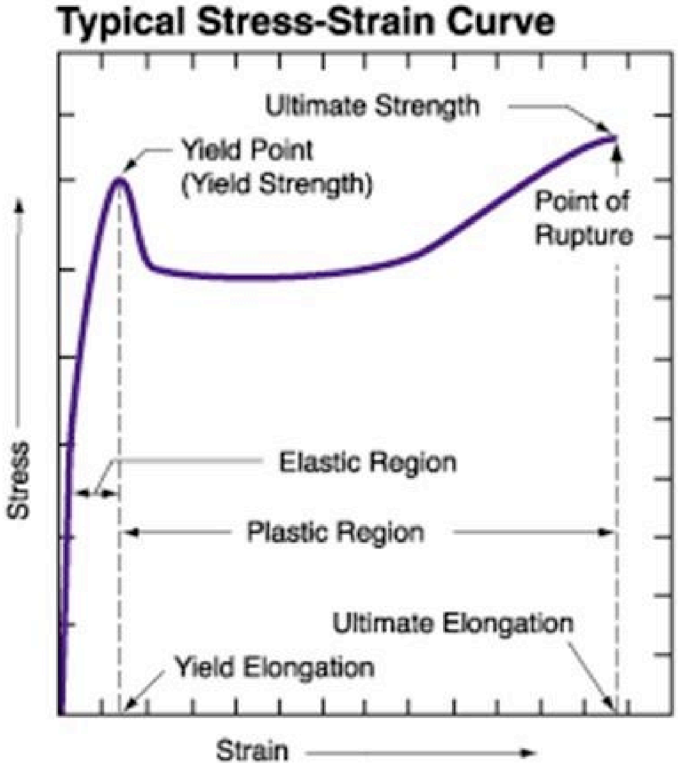


http://www.greatdreams.com/political/non-orwell-zebra.htm

Elastic materials

Tensile test

Thermoplastic polymer



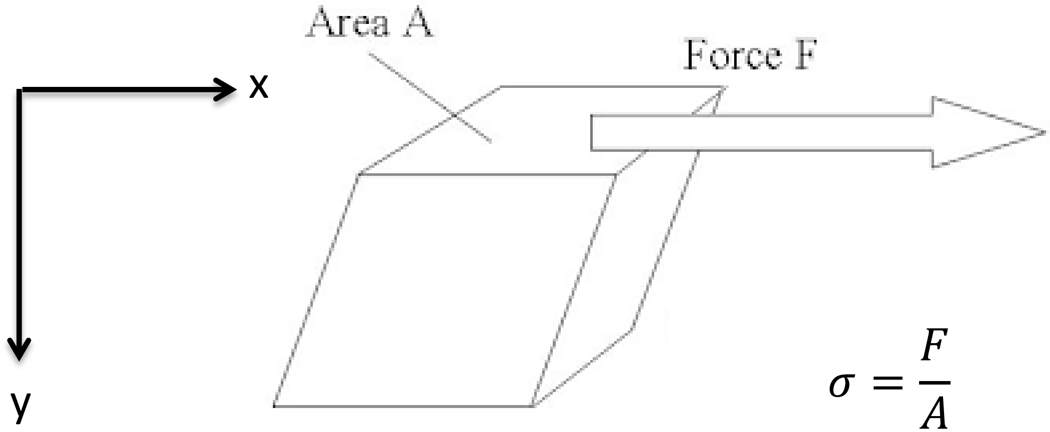
http://www.kazuli.com/UW/4A/ME534/lexan2.htm

Viscous or viscoelastic materials

rheology

Rheology

The shear and storage moduli of polymers can be characterized with rheology.



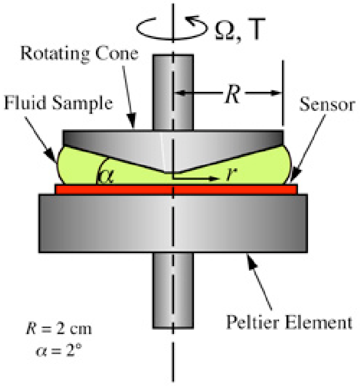
$$\tau = \dot{\gamma}\eta$$

$$\dot{\gamma} = \frac{dv_x}{dy}$$

$$\sigma = \frac{F}{A}$$

$$\tau = \eta\frac{dv_x}{dy}$$

τ: shear stress [Pa]
η: viscosity [Pas]
v: velocity [m/s]
F: force [N]
A: area [m^2]
$\dot{\gamma}$: shear rate [s^{-1}]

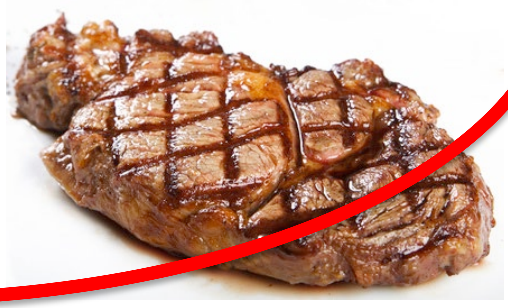


1. mode of operation:
The top geometry of the rheometer rotates at a defined $\dot{\gamma}$ and you measure the stress required to reach this value.

2. mode of operation:
The top geometry of the rheometer rotates with a defined τ and you measure the resulting $\dot{\gamma}$.

See also course "Rheology and fluid mechanics" by Yves Leterrier MSE-206

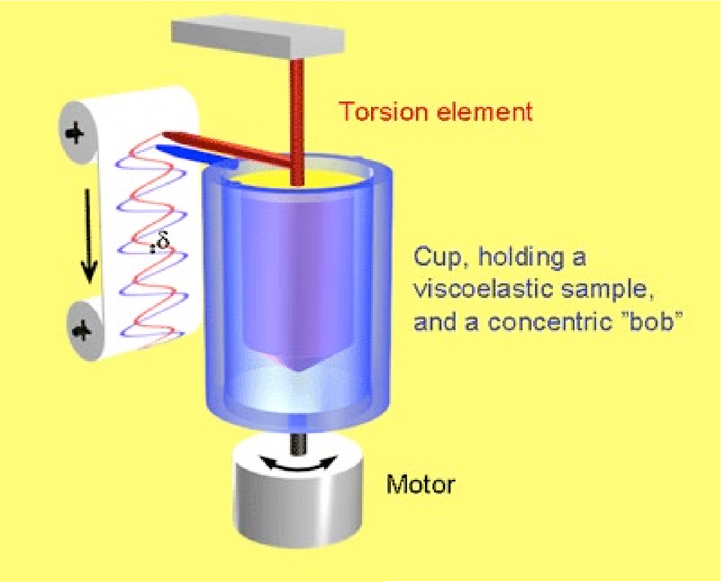
Viscous or viscoelastic materials

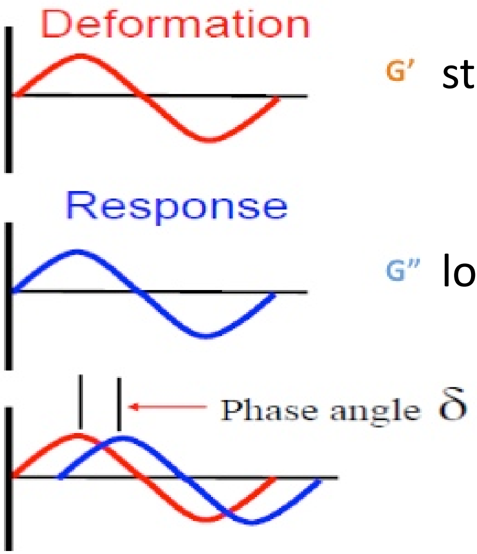


rheology

Oscillatory Rheology

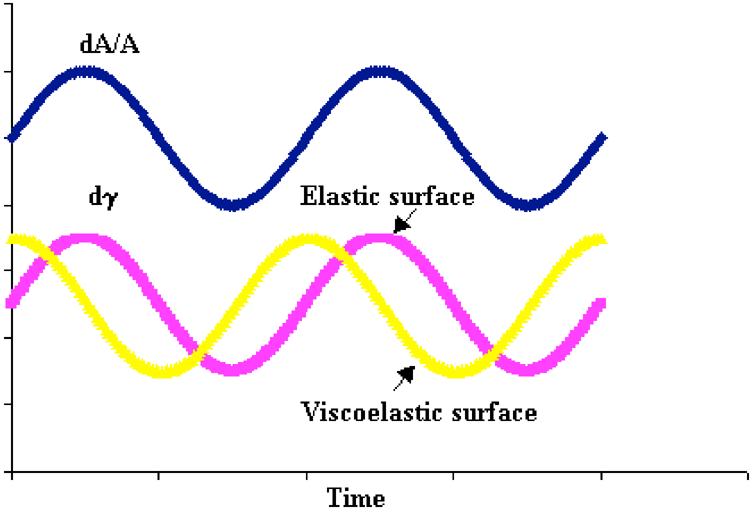
Viscoelastic materials are often characterized with oscillatory rheology:





G′ storage modulus

G″ loss modulus



Oscillatory Rheology

Viscoelastic materials are often characterized with oscillatory rheology:

$$\gamma = \gamma_0 \sin(\omega t)$$

δ: loss tangent, measures energy loss per cycle [rad]

$$\sigma = \sigma_0' \sin(\omega t) + \sigma_0'' \cos(\omega t)$$

$$\sigma = G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t)$$

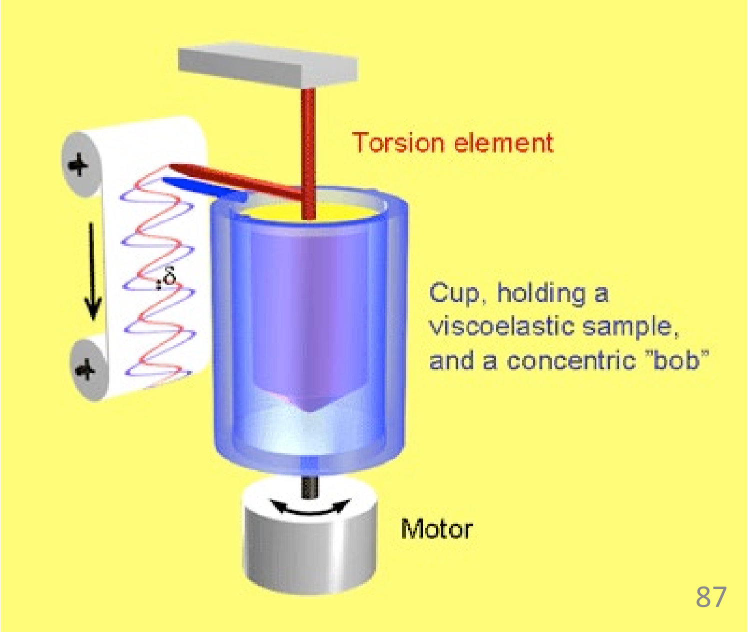
$$\tan\delta = \frac{G''}{G'}$$

storage modulus

$$G' = \frac{\sigma_0'}{\gamma_0}$$

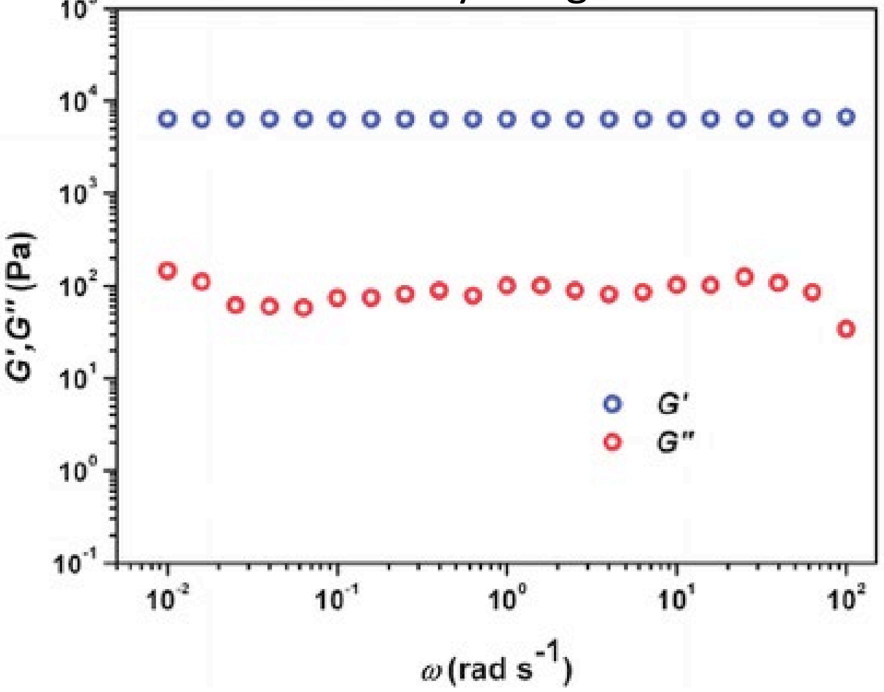
loss modulus

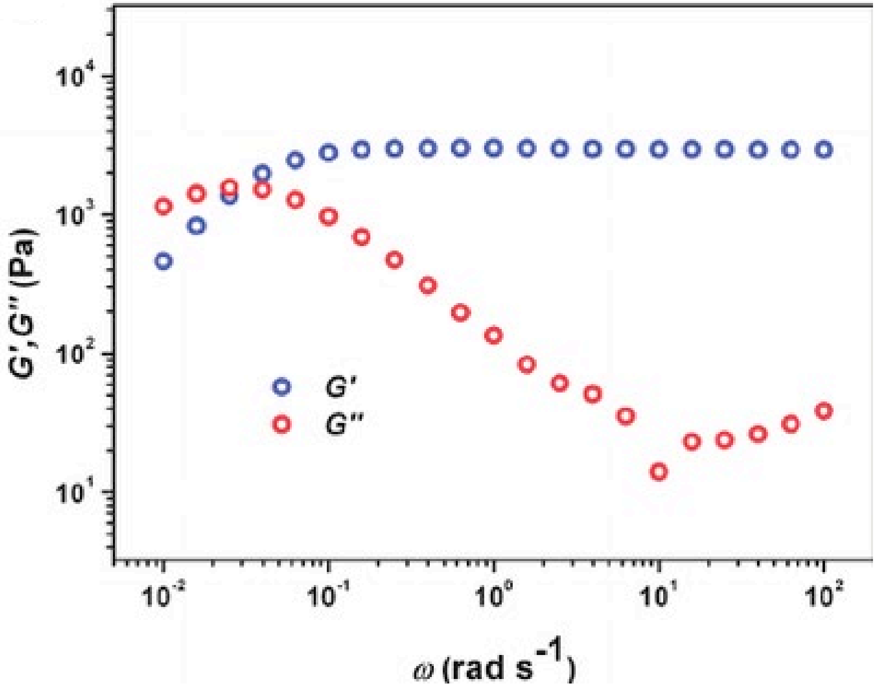
$$G'' = \frac{\sigma_0''}{\gamma_0}$$



Rheology on polymer gels

bis-acylhydrazine functionalized poly(ethylene oxide)


Polymer gel


Polymer gel after 3 sol-gel transitions

G. Deng, C. Tang, F. Li, H. Jiang and Y. Chen, *Macromolecules*, 2010, **43**, 1191-1194

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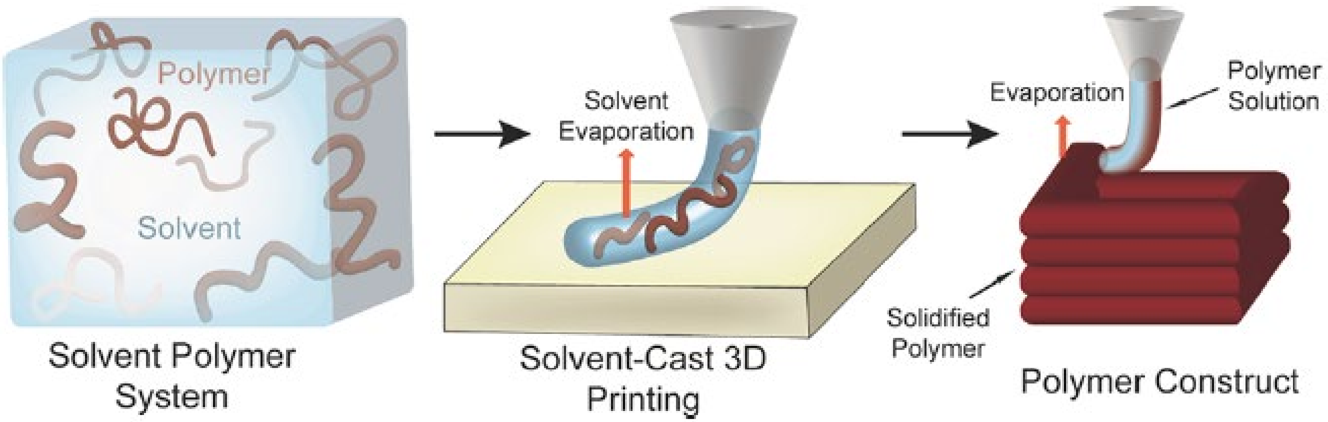
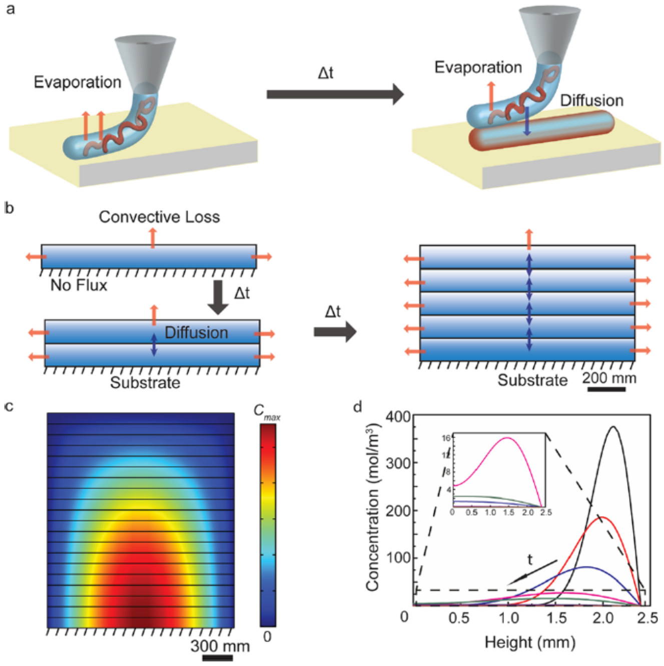
3D printing of polymer solutions





Singh, M.; et al., *ACS Appl. Mater. Interfaces* **2019**, *11* (6), 6652–6661.