Polymers in Soft Matter: From Structure to Emerging Applications

Part 1: Polymer Structure and Theoretical Models

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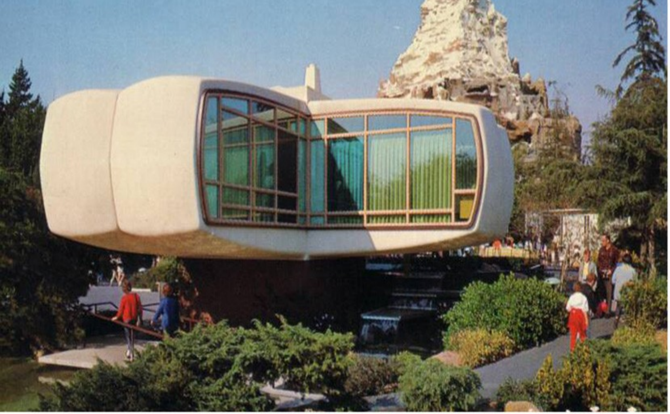
”You Either Die A Hero, Or You Live Long Enough To See Yourself Become The Villain“




”You Either Die A Hero, Or You Live Long Enough To See Yourself Become The Villain“

Celluloid (1869) and Bakelite (1909)

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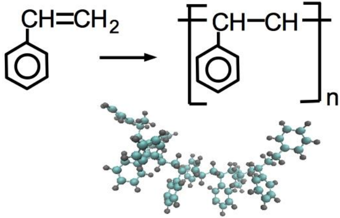
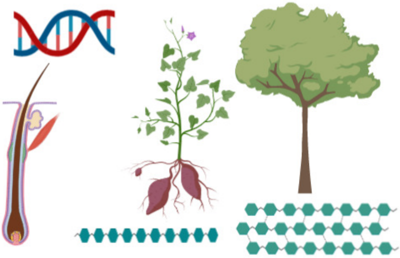
What is polymer?

- macromolecule consisting of monomers
- prepared by polymerization
- degree of polymerization *n*



→ Synthetic

→ Biopolymers



*the picture was created with BioRender

Thermoplastics, thermosets, elastomers

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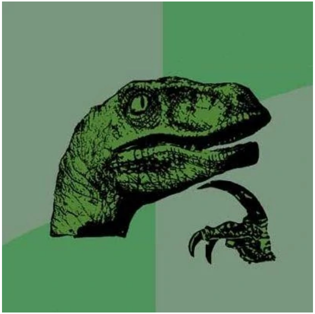
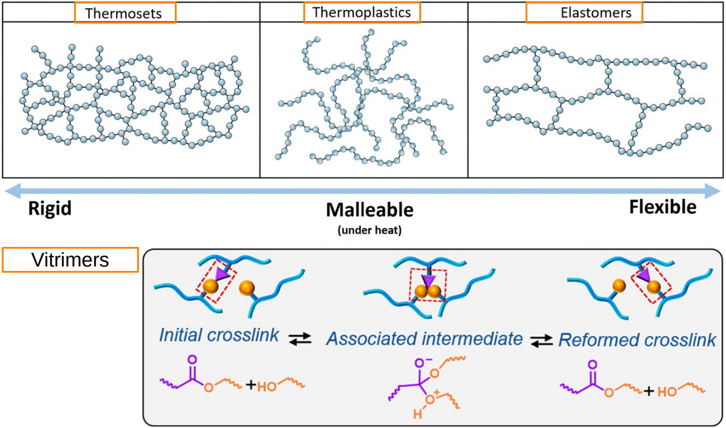


Find one key property which commercial polymers have in common

Thermoplastics, thermosets, elastomers



[1] Cuttaz, E. A. et al.; Adv. Healthcare Mater. 2024, 13, 2304447
[2] Chen, Q.; Yang, Y.; Yu, Y.; Xu, H.; Journal of Chemical Education 2021 98 (4), 1429-1435

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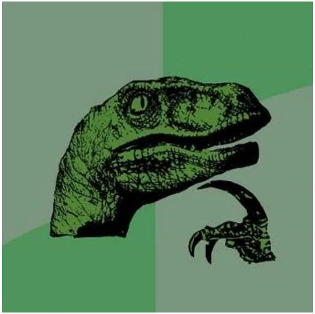
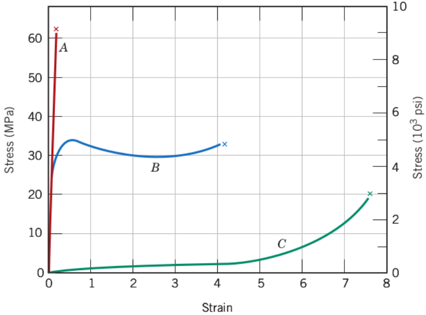
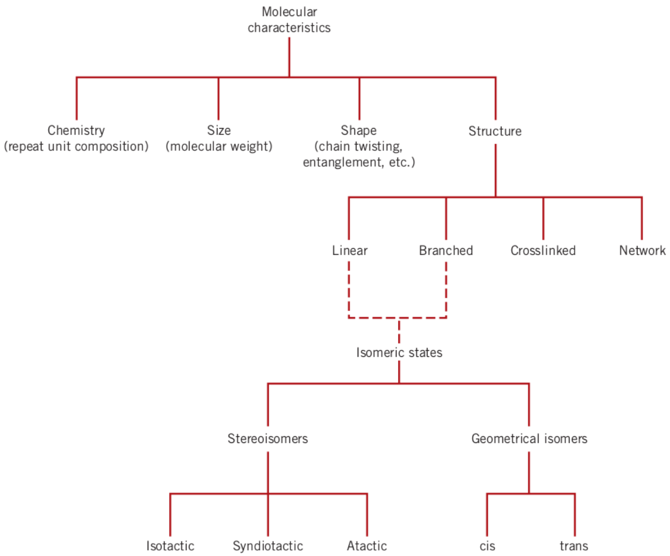
INNANOMAT MATERIALS FOR INNOVATION



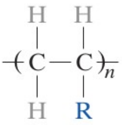


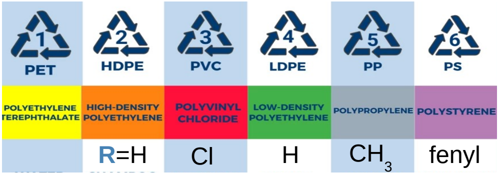
Which stress-strain curve belongs to elastomer, thermoset and thermoplastic?

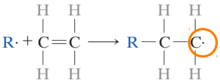


[1] Callister, W. D., Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Hoboken, NJ: Wiley

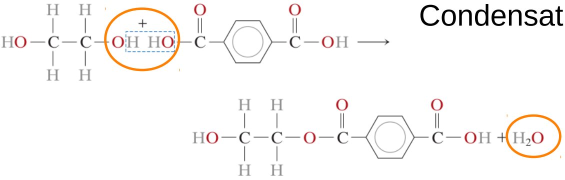
Polymer chemistry







Addition

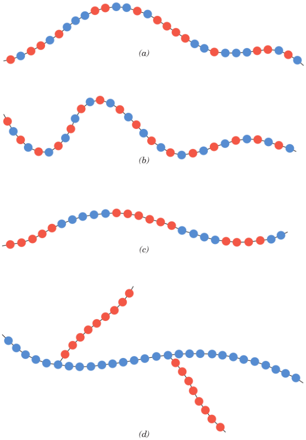


Condensation

[1] Callister, W. D., Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Hoboken, NJ: Wiley

Type of monomer units

- Homopolymers
- Copolymers
  - (a) random
  - (b) alternating
  - (c) block
  - (d) graft



Most popular copolymers:

- Acrylonitrile Butadiene Styrene (ABS)-Lego
- Styrene-Butadiene Rubber (SBR)-tires
- Nylon 6,6-parachutes

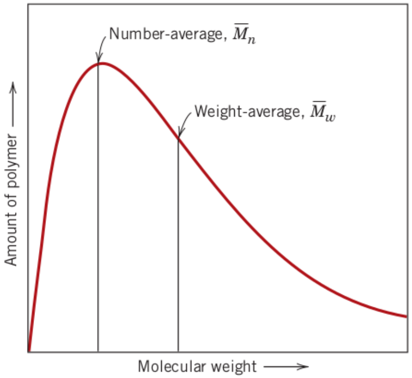
[1] Callister, W. D., Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Hoboken, NJ: Wiley

Molecular weight

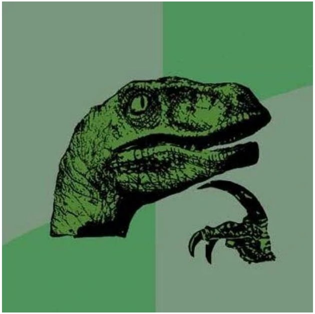
- number-average M_n vs. weight average M_w
- monodisperse vs. polydisperse samples, PDI=M_w/M_n
- non-entangled vs. entangled

→ one of the most important characteristics

- viscosity $\sim M_w^\alpha$
- thermal properties M_w dependent

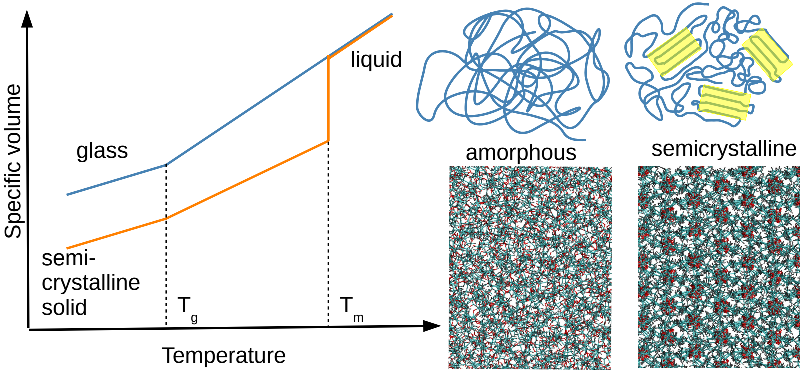


[1] Callister, W. D., Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Hoboken, NJ: Wiley



Guess an average molecular weight of commercial polymers

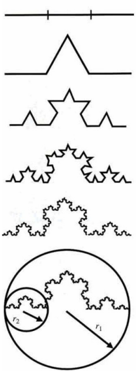
Amorphous and semicrystalline polymers

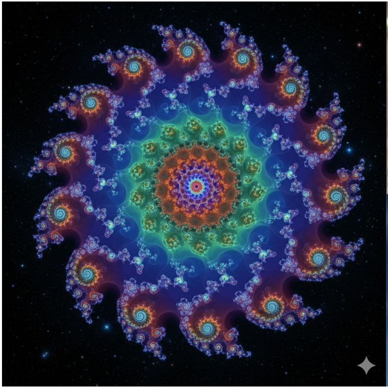


→ T_g glass transition temperature

→ T_m melting temperature

Fractal character

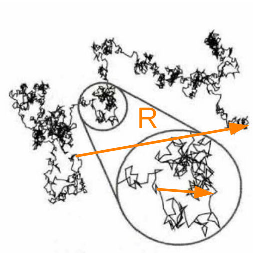


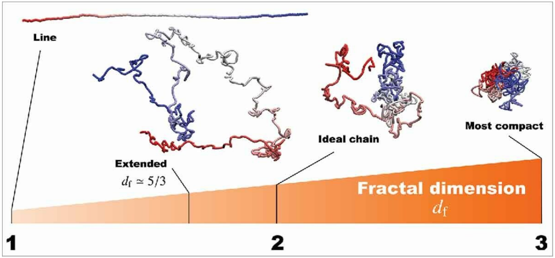


- self-similar over a wide range of length scales
- fractal dimension

Fractal character of polymers

- $g \sim (\sqrt{\langle R^2 \rangle})^{d_f}$, g number of monomers in a subsection

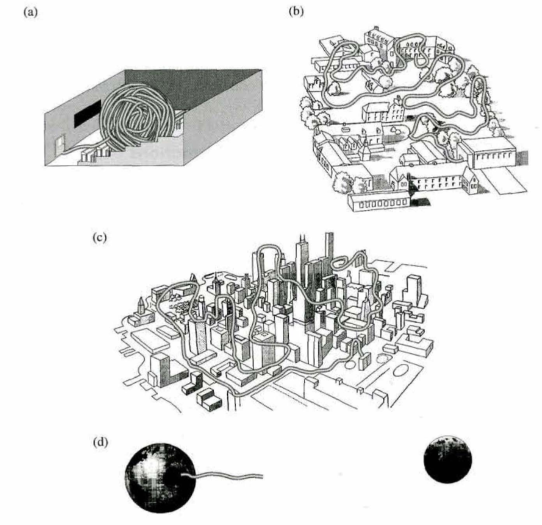




!!! configuration highly dependent on environmental factors (temperature, solvent quality, confinement, ionic strength) and intrinsic characteristics (stiffness, internal H-bonding)

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.
[2] Shinkai, S., Nozaki, T., Maeshima, K., Togashi, Y. (2017). Nucleus, 8(4), 353–359.

Fractal character of polymers



$g = 10^{10}$, size 1 cm

(a) attractive interactions

(b) zero effective interaction

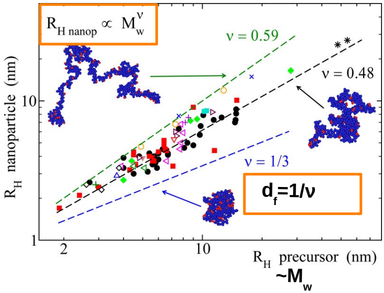
(c) short-range repulsion

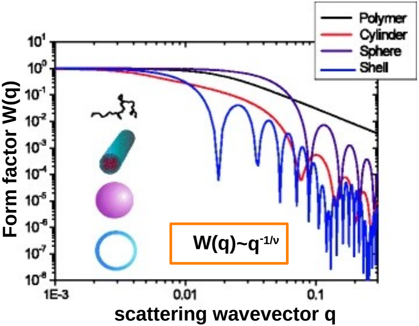
(d) long-range repulsion

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Fractal character of polymers

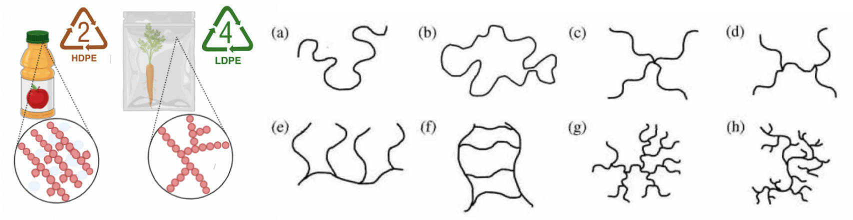
- single-chain form factor $W(q) = \langle \frac{1}{N^2} \sum_{j,k}^{N} \exp(-i\vec{q}(\vec{R}_j - \vec{R}_k)) \rangle$





[1] Pomposo, J. A.; Perez-Baena, I.; Lo Verso, F.; Moreno, A. J.; Arbe, A.; Colmenero, J.; ACS Macro Letters 2014 3 (8), 767-772
[2] Lund, R., Willner, L., Richter, D. (2013). Controlled Polymerization and Polymeric Structures. Advances in Polymer Science, vol 259. Springer, Cham.

Polymer architecture

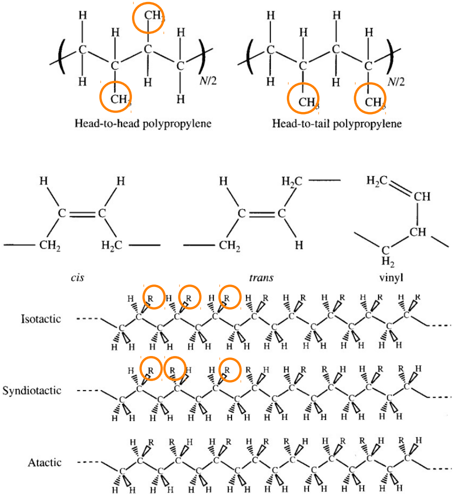


- HDPE: higly crystalline, stiff, hard, high tensile strength
- LDPE: flexible, soft, high toughness and impact strength

(a) linear
(b) ring
(c) star
(d) H
(e) comb
(f) ladder
(g) dendrimer
(h) random branching

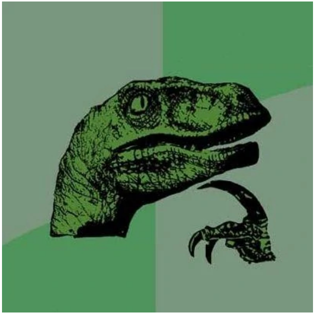
[*] picture created by BioRender
[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Polymer microstructure



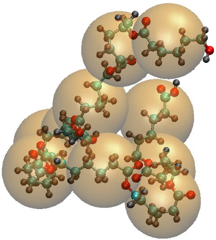
- cis, trans and vinyl PB differences in T_m, crystallinity and applications
- iPP highly crystalline
- sPP lower crystallinity than iPP
- aPP amorpohous

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

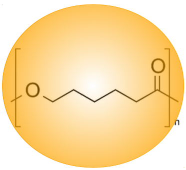


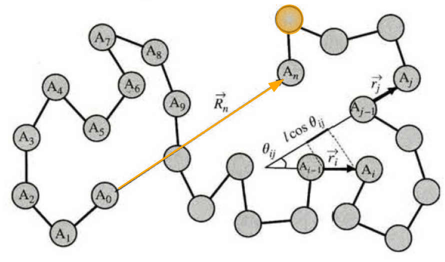
Find other commercial polymers, which have different stereoisomers.

Theoretical models for polymers



PCL





- infinite chain with Gaussian statistics
- no microstructure, coarse-grained picture
- chemistry-independent

→ correct prediction of the large-scale behavior of most real polymers in certain conditions, regardless of their specific chemical structure

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Theoretical models for polymers

Parameters

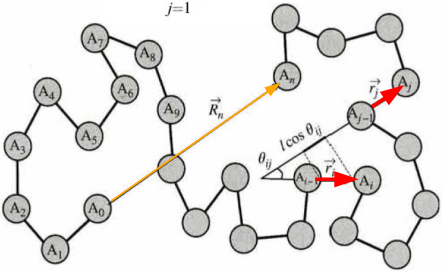
- local stiffness
  - characteristic ratio
  - Kuhn length
  - persistence length
- size: radius of gyration, end-to-end distance
- characteristic times
- other characteristics: T_g, T_m, plateau modulus etc.

Conformation of an ideal chain

$$\langle R^2 \rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \vec{r}_i \cdot \vec{r}_j \rangle = l^2 \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \cos\theta_{ij} \rangle$$

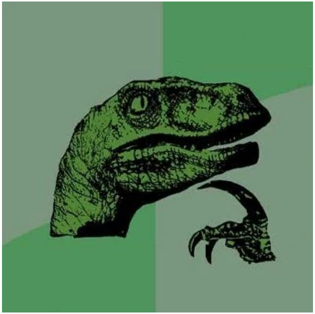
$$\langle R^2 \rangle = l^2 \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \cos\theta_{ij} \rangle = l^2 \sum_{i=1}^{n} C'_i = C_n n l^2$$

$$C'_i \equiv \sum_{j=1}^{n}\langle \cos\theta_{ij} \rangle$$



- fix bond length l
- correlations in local conformation expressed through cosine
- if $\langle \cos\theta_{ij} \rangle = 0$ when $i \neq j$ no correlation
- end-to-end vector: if $n = N \Rightarrow R_n = R$
- characteristic ratio: if $lim_{n\to\infty} C_n = C_\infty$

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

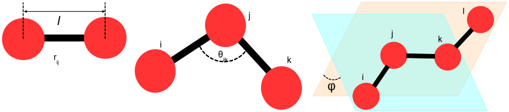


Why in an ideal isotropic system of multiple chains consisting of n atoms $\langle \vec{R}_n \rangle = 0$?

Ideal models

Flory's characteristic ratio

$$\langle R^2 \rangle = C_\infty n l^2$$

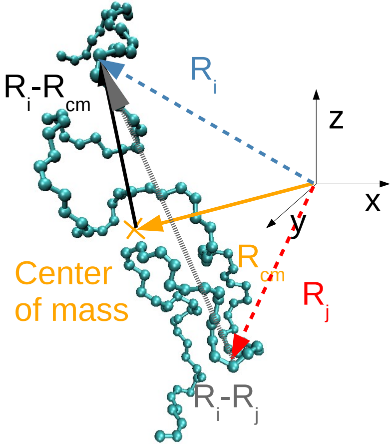


Models	FJC	FRC	HR
Bond length l	Fixed	Fixed	Fixed
Bond angle θ	Free	Fixed	Fixed
Torsion angle φ	Free	Free	Controlled by $U(\varphi)$
Next φ independent?	Yes	Yes	Yes
C_∞	1	$\frac{1+\cos\theta}{1-\cos\theta}$	$\left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\theta\rangle}{1-\langle\cos\varphi\rangle}\right)$

- FJC freely jointed chain
- FRC freely rotating chain
- HR hindered rotation

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Radius of gyration of an ideal chain



- definition:

$$R_g^2 = \frac{\sum_i^N m_i (R_i - R_{cm})^2}{\sum_i^N m_i}$$

- if all m_i equal:
  $\langle R_g^2 \rangle = \frac{1}{N} \sum_i^N \langle (R_i - R_{cm})^2 \rangle$
- $\langle R_g^2 \rangle = \frac{1}{N^2} \sum_i^N \sum_j^N \langle (R_i - R_j)^2 \rangle$

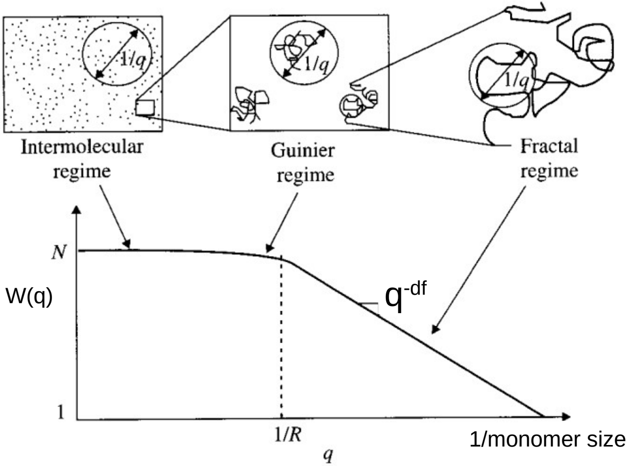
For flexible, Gaussian chains:

$$\langle R_g^2 \rangle = \frac{\langle R^2 \rangle}{6}$$

$\Rightarrow$ indicates ideal behaviour

Scattering Techniques for Polymer Characterization

- $W(q) = \langle \frac{1}{N^2} \sum_{j,k}^{N} \exp(-i\vec{q}(\vec{R}_j - \vec{R}_k)) \rangle$ $\quad q = \frac{4\pi}{\lambda} \sin(\theta/2)$



Scattering Techniques for Polymer Characterization

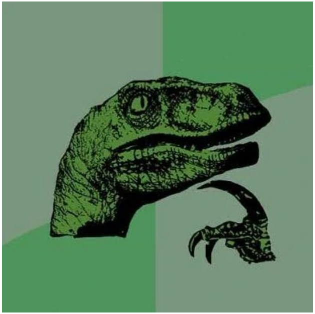
- Small-Angle X-ray Scattering (SAXS): electron density contrast
- Small-Angle Neutron Scattering (SANS): contrast in scattering length density, often enhanced by deuteration
- Static Light Scattering (SLS): suitable for large polymers

$\Rightarrow$ estimation of R_g, Guinier function

$$W(q) \cong \exp\left(-\frac{q^2 R_g^2}{3}\right) \quad qR_g < 1$$

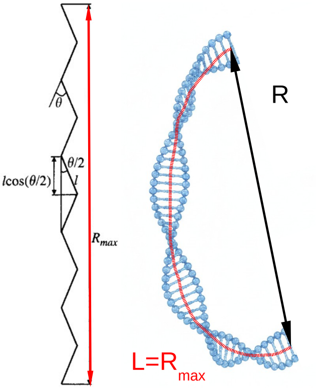
+ estimation of aggregation, deformation..

- Ideal linear chains: form factor expressed by Debye function



Suggest a way to collect the scattering from only one molecule

Worm-like chain model



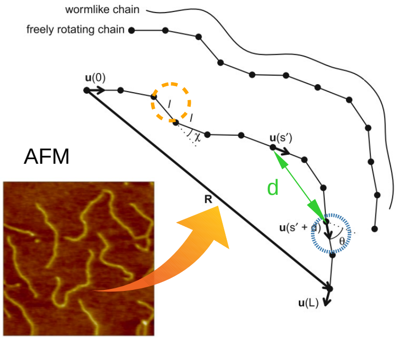
- Kratky-Porod model
- freely rotating chain with small θ angle
- flexibility related to the fluctuations of the contour length R_{max}
- semiflexible/stiff polymers
- persistence length significant in comparison to the total chain length

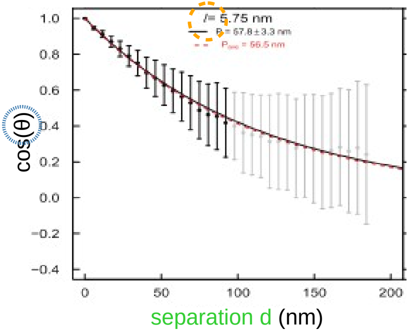
$$\langle R^2 \rangle = 2 l_p \langle R_{\mathrm{max}} \rangle \left(1 - \frac{l_p}{\langle R_{\mathrm{max}} \rangle}\left[1 - \exp(-\langle R_{\mathrm{max}} \rangle / l_p)\right]\right)$$

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Kuhn length b, persistence length l_p

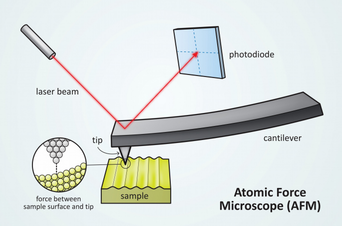
$$\langle \cos\theta(d) \rangle = \frac{\vec{u}_i . \vec{u}_{i+d}}{|\vec{u}_i||\vec{u}_{i+d}|} = \exp(-d/l_p), \qquad \text{For WLC} \quad b = 2l_p$$

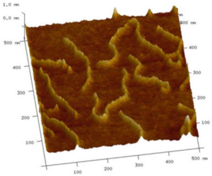




[1] Peters, J.P., Maher III, L.J. (2024). Approaches for Determining DNA Persistence Length Using Atomic Force Microscopy. In: Dame, R.T. (eds) Bacterial Chromatin. Methods in Molecular Biology

Atomic Force Miscroscopy

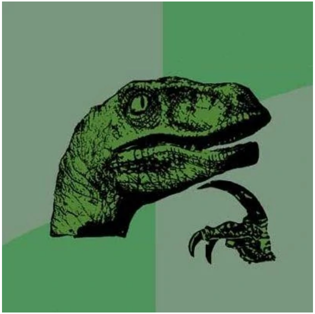




- three-dimensional (3D) maps of the polymer surface
- non-destructive
- possibility of measuring mechanical properties
- operability in diverse environments

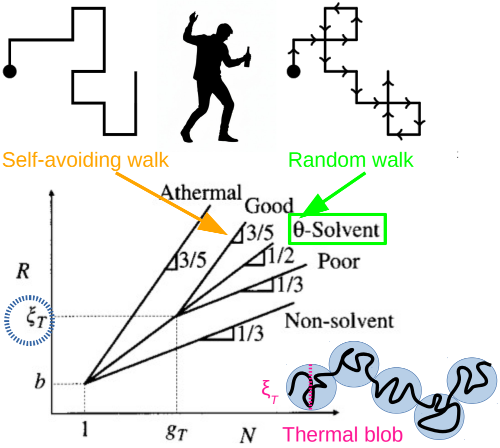
!! No bulk information

[1] Peters, J.P., Maher III, L.J. (2024). Approaches for Determining DNA Persistence Length Using Atomic Force Microscopy. In: Dame, R.T. (eds) Bacterial Chromatin. Methods in Molecular Biology



Your task is to measure the polymer characteristics via AFM. In your opinion, what is the single most critical factor influencing your measurements?

Real Chains

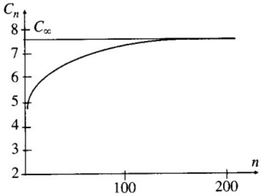


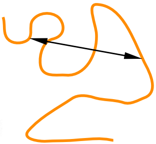
- excluded volume
- thermal blob size ξ_T, EV weaker than kT
- swollen, ideal and collapsed conformations
- θ solvent: ideal conformation
- melt: screened interactions

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Chain flexibility: Characteristic ratio

Polymer	C_∞
polypropylene	5.9
atactic polystyrene	9.5
polyethylene	7.4
1,4-polyisoprene	4.6



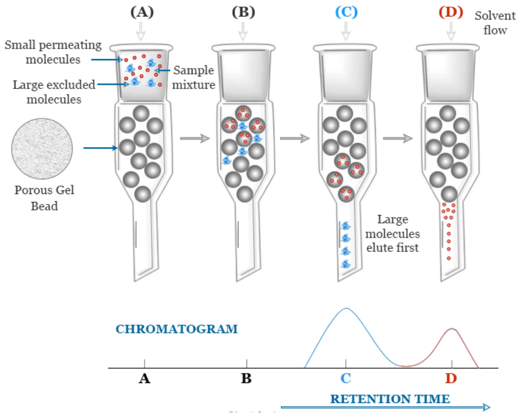


- chain-length dependent
- $\langle R^2 \rangle = C_\infty n l^2$, $C_\infty = \langle R^2 \rangle / n l^2$
- measurements of R^2 in θ-conditions
- Viscometry: Stockmayer–Fixman equation to extrapolate to ideal conditions, K_Θ proportial to R^2

$$\frac{[\eta]}{M^{1/2}} = K_\Theta + B' M^{1/2}$$

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Gel Permeation Chromatography



- separation based on hydrodynamic volume
- elution time correlated with molecular weight
- calibration to standards or GPC-SLS combination

[1] https://www.priyamstudycentre.com/2022/02/gel-permeation-chromatography.html

Keep calm and stay tuned!

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☞ https://polysim.eu/

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