Physics 850: Soft Condensed Matter Physics, Fall04
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Lecture 5: Polymers

Polymers

(Kleman ch 15)
(Rubenstein & Colby Polymer Physics)

Polymer = "molecule of high molecular mass composed of many small structural units connected by strong covalent bonds"

Types:
homopolymers – units are identical
copolymers – > 1 type of monomer
random copolymers – units vary randomly
block copolymers – units are identical in sections
(di – 2 blocks
tri – 3 blocks)

linear: each unit has 2 bonds (except ends)
branched, ring, star, dendrimer, comb, ladder, ...

Degree of polymerization

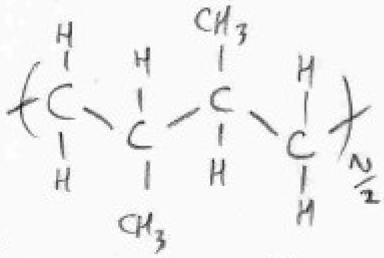
Examples of linear ~~homo~~polymers

≈1.5 Å

polyethylene $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdots = CH_3 \left(CH_2 \right)_N CH_3$

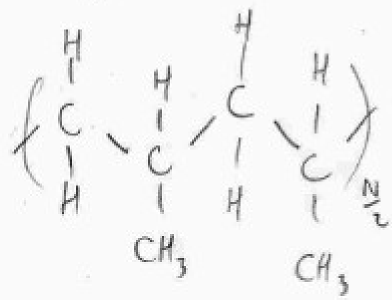
(plastic bags)

polypropylene:



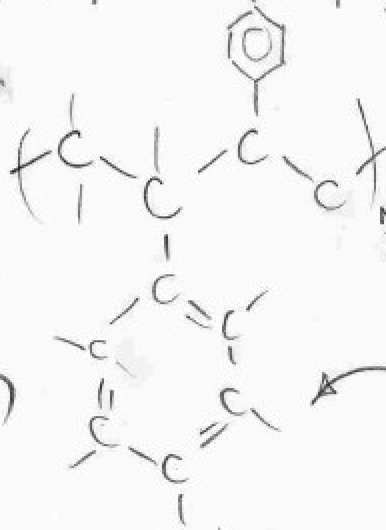
sequence isomers

or



polystyrene: (replace CH_3 of polypropylene with C ring)

e.g.



(plasticware, styrofoam: often cross linked)

sometimes an ionic groups is here (e.g. polystyrene sulfonate, H_2O soluble

(PEG)

polyethylene oxide, poly ethylene glycol, poly-oxy-ethylene.

$$\left[CH_2 - CH_2 - O \right]_n$$

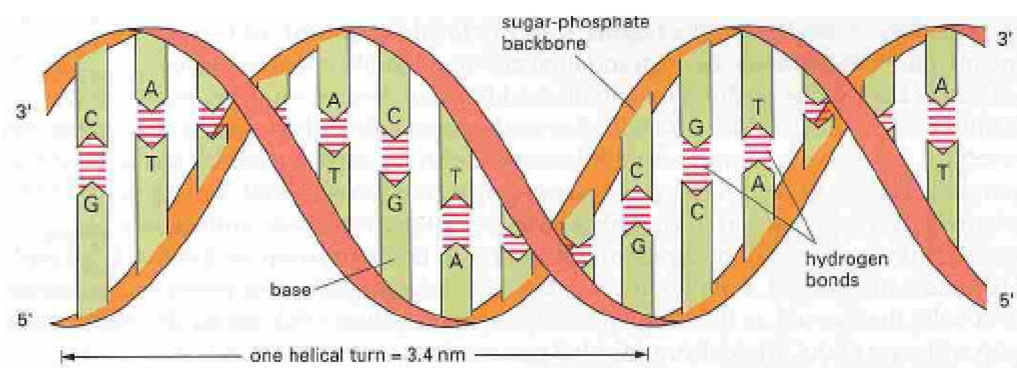
↑ makes it water soluble

polydimethyl siloxane (PDMS)

$$Si - O \left[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}} - O \right] Si$$

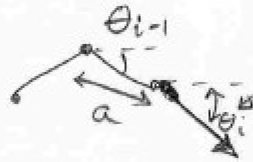
(silicone rubber)

Double-stranded DNA: a (pseudo) random copolymer with 4 bases: A, G, C, and T. Kuhn length ~ 100 nm (much larger than polyethylene's 1.4 nm).



A simple model: Ideal (Gaussian) chain
(Freely jointed chain)

→ Assume polymer is composed of N segments of length a, which do not interact and are independent (except by being connected)

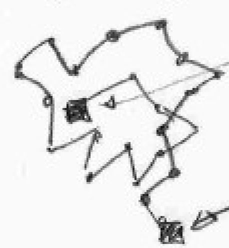


θ_i is independent of θ_{i-1}

- Each junction is a freely pivoting hinge
- $\hat{t}_i$ is direction of i^{th} segment

→ contour length = Na

→ Average lengths:



Let this end sit at origin

this end at $(x, y, z) = \vec{r}$

$$\vec{r} = \sum_{i=1}^{N} a\,\hat{t}_i$$

$\langle \vec{r} \rangle = aN \langle \hat{t} \rangle = 0$ because θ_i is random

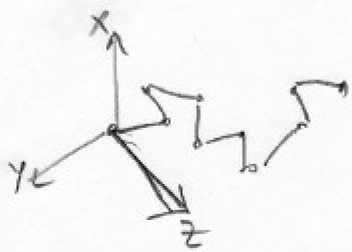
$$\langle r^2 \rangle = \left\langle \left(a \sum_i \hat{t}_i\right) \cdot \left(a \sum_j \hat{t}_j\right) \right\rangle = a^2 \left\langle \sum_{i,j=1}^{N} \underbrace{\hat{t}_i \cdot \hat{t}_j}_{= \delta_{ij}} \right\rangle$$

only N terms with $i = j$ contribute.

so $\boxed{\langle r^2 \rangle = Na^2}$

Central-Limit-Theorem (cf. Kleman §15.1)

or Random-Walk view:



x = end-to-end length of polymer along x-axis

y = " " y-axis

z = " " z-axis

$$P(x,y,z) = (\text{const.})\, e^{-\frac{(x-\langle x\rangle)^2}{2\sigma_x^2}}\, e^{-\frac{(y-\langle y\rangle)^2}{2\sigma_y^2}}\, e^{-\frac{(z-\langle z\rangle)^2}{2\sigma_z^2}}$$

$\rightarrow \langle z\rangle = \langle x\rangle = \langle y\rangle = 0$ (polymer equally likely to fluctuate to L or R)

so $(x-\langle x\rangle)^2 = x^2$

and $\sigma_x = \langle x^2\rangle$

$\rightarrow \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = \langle r^2\rangle \rightarrow \langle x^2\rangle = \frac{\langle r^2\rangle}{3} = \langle y^2\rangle$.

$$P(r) = (\text{const})\, e^{-\frac{r^2}{2(\langle r^2\rangle)/3}}, \text{ where } r^2 = x^2+y^2+z^2$$

$$= (\text{const.})\, e^{-\frac{3r^2}{2\langle r^2\rangle}}$$

Since $P(r) \propto e^{-\frac{F(r)}{k_BT}} \rightarrow F(r) = F_0 + \frac{3k_BT\,r^2}{2\langle r^2\rangle}$

$\rightarrow \langle r^2\rangle = a^2 N$

so $F(r) = F_0 + \frac{3k_BT\,r^2}{2a^2N}$

force exerted by polymer $= \frac{-\partial F(r)}{\partial r} = -\left(\frac{3k_BT}{a^2N}\right) r$ — spring constant

Corrections to Ideal chain model

1) What is the random walk length?
(Kuhn length, b)

linear hydrocarbon polymers rotate by
alternation between trans & gauche
(Kleman fig 15.1)

Polyethylene:
C-C bond length $\simeq 1.5$ Å

Kuhn length, b $\simeq$ 14 Å because of correlations

Trans-gauche variations in structure give rise to bends – see Kleman

DNA (double helix)

$b \simeq 100\,nm$ (70x larger than PE)

2) Excluded volume: 2 chain segments cannot overlap

Result: $\sqrt{\langle r^2 \rangle} = a \cdot N^{3/5}$ (not $\frac{1}{2}$, as in ideal model)

(Flory theory)