Solution to HW #1

Q1. For TGTG'G'TG'TTG conformation of n-$C_{13}H_{28}$ with bond angle of 120° and bond length of 1 cm,

(1) Find the end-to-end distance. ~ 7 cm

(2) C? $7^2/12$

Q2. Using the energy values given so far, estimate the probability of GG' conformations in n-pentane at 350 K

(1) for independent ϕ's

U(TT)=(1)(1)=1, U(TG,TG',GT,G'T)=(1)(σ)=σ,
U(GG,GG',G'G,G'G')=(σ)(σ)= σ^2, σ=exp(-2.1/kT)~.49

$P(GG') = U(GG')/Z = \sigma^2/(1+4\sigma+4\sigma^2) = .06$

(2) for interdependent ϕ's

U(TT)=1, U(TG,TG',GT,G'T)=σ, U(GG,G'G')=(σ)($\sigma\psi$)=exp(-4.2/kT)=.24,
U(GG',G'G)=(σ)($\sigma\omega$)=exp(-14.5/kT)=.007,

$P(GG') = U(GG')/Z = \sigma^2\omega/(1+4\sigma+2\sigma^2\psi+2\sigma^2\omega) = .002$

Solution to HW #1

Q3. For *n*-octane,

(1) how many conformations? 3^5

(2) Express the probability of TTTTT.

$\Omega = \Pi \, U_{\zeta\eta} = U(T)U(TT)U(TT)U(TT)U(TT) = 1$

$Z = \Sigma \, \Pi \, U_{\zeta\eta} = 1 + \text{-----}$

$P = 1/Z$

(3) Express the probability of TGG'TG.

$\Omega = \Pi \, U_{\zeta\eta} = U(T)U(TG)U(GG')U(G'T)U(TG)$

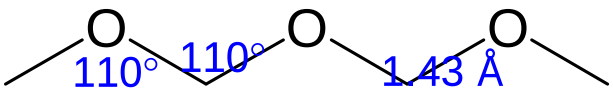
$= (1)(\sigma)(\sigma\omega)(1)(\sigma) = \sigma^3\omega$

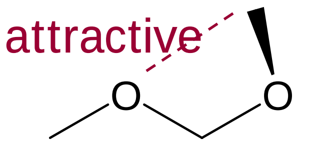
$P = \sigma^3\omega/Z$

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix}$$

Polyoxymethylene

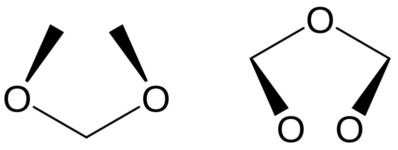
- geometry and interactions
  - one type θ and l → a simple chain → one **T**
  - 3-bond interaction
    - » D(C-O) < D(C-C) of PE → larger E_{kl}(G)
    - » attractive C---O interaction → E_d(G) <0
    - » E_{kl}(G) < E_d(G) → E_{tot}(G) < 0 → σ >1





$$\mathbf{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix}$$

- stat wt
  - 1^{st}-order, **D** ~ with σ > 1
  - two 2^{nd}-order matrices ~ $\mathbf{V}_a$ for C---C, $\mathbf{V}_b$ for O---O
  - $\mathbf{U}_a = \mathbf{D}\,\mathbf{V}_a$, $\mathbf{U}_b = \mathbf{D}\,\mathbf{V}_b$



POM (2)

- results
  - $C_\infty = 8$

    with $\sigma =$ 10, ω = 0.05

    experiment difficult ~ high melting and low solubility
  - $d[\ln \langle r^2 \rangle_o] / dT < 0$

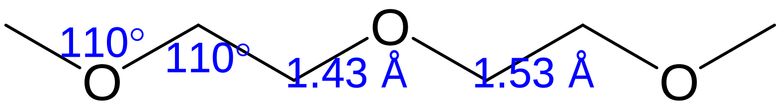
    $T \uparrow \rightarrow \sigma \downarrow \rightarrow C_\infty \downarrow$

    $\sigma \downarrow \rightarrow P(T) \downarrow$ ~ More trans gives lower dimension?

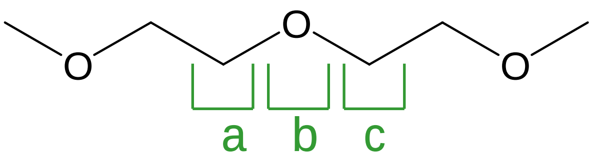
- preferred conformation
  - GGGG---- or G’G’G’G’----
  - 2_1 helix (ϕ(G)=117°) or 9_5 helix (ϕ(G)=102°) in crystal

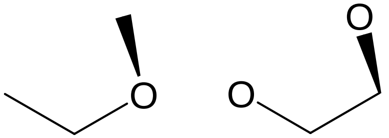
Polyoxyethylene

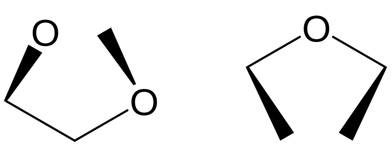
- geometry and interactions
  - one θ and two l → one **T**?
  - R(O) < R(C)
  - do have dipole
    - » but no attractive interaction, all repulsive



- stat wt
  - Three **U**'s
  - 1st-order
    - » $\mathbf{D}_a = \mathbf{D}_b$ (C---C) ~ with $\sigma < .5$
    - » $\mathbf{D}_c$ (O---O) ~ $\sigma' < 1$
  - 2nd-order matrices
    - » $\mathbf{V}_a = \mathbf{V}_c$ (C---O) ~ with $\omega > 0$
    - » $\mathbf{V}_b$ (C---C) ~ $\omega \approx 0$







PEO (2)

- results
  - $C_\infty = 4$

    with σ = .26, ω = 0.6, σ' = 1.9 (E(σ') = -1.7 kJ/mol)

    best fit to exp't

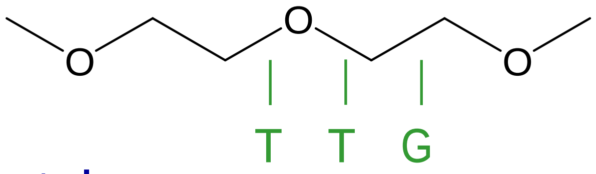
    why $\sigma' > 1$?

    reason not clear, maybe related to very large σ in POM

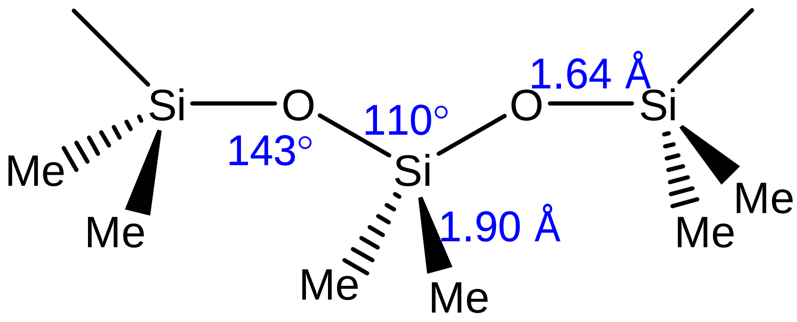
    Oxygen lower the energy of gauche (preferred over trans)
  - TC = 2.3E-4

    T ↑ → σ, ω ↑, σ' ↓ → C_∞ ↑

- preferred conformation
  - TTGTTG---
  - 7_2 helix (ϕ(G)= -8°, ϕ(G)=115°) in crystal

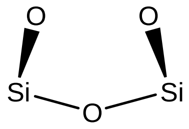


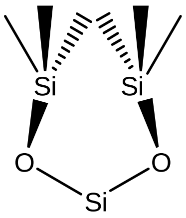
Poly(dimethyl siloxane)



- geometry and interactions
  - two θ's → two **T**'s
  - large D(Si-O), D(Si-C)
    - → large r_{kl} → low E_{kl} and E^0
    - → low E(G) → RIS not well-defined

- stat wt
  - two **U**'s ← one **D** and two **V**'s
  - $\omega > 0$
  - $\omega' \approx 0$

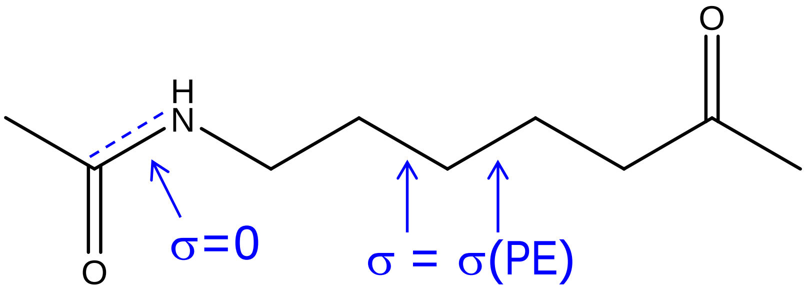




- results
  - C_∞ = 6.2, TC = 7.8E-4
    with σ = .29, ω = 0.2

Polyamides

- nylon 6
  - 7 **U**'s
  - $\mathbf{U}_1 = 1$
  - $\mathbf{U}_2 = [1\ \sigma_2\ \sigma_2]$
  - $\mathbf{U}_3$ --- $\mathbf{U}_7 \sim 3 \times 3$
  - $\sigma_4 = \sigma_5 \sim \sigma$ in PE ~ .5
  - other σ's > .5; ω's > 0
    - » R(O, N) < R(C)
    - » NH favors gauche like O
  - use avg length
  - $C_\infty \sim 6$



Polyesters

- PET
  - 6 **U**'s
  - $\mathbf{U}_1 = 1$
  - $\mathbf{U}_2 = [1\ \gamma]$

    $\approx \gamma \sim 1$ ← long virtual bond
  - $\mathbf{U}_3 = 1$
  - $\mathbf{U}_4 = [1\ \sigma_4\ \sigma_4]$
  - $\mathbf{U}_5$, $\mathbf{U}_6 \sim 3 \times 3$
  - $\sigma_4 = \sigma_6 \sim \sigma$ in PE ~ .5
  - $\sigma_5 \sim \sigma$ in PEO > 1
  - two σ's and one ω
  - $C_\infty \sim 4$