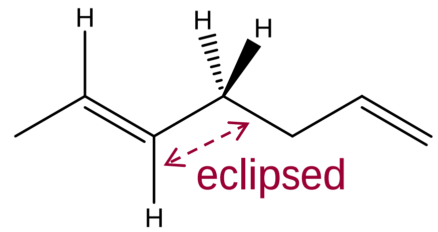
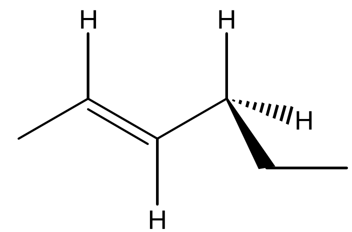
Polymers with C=C

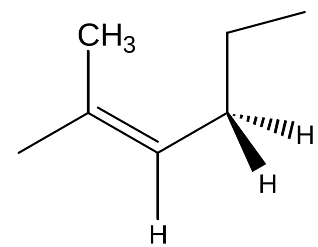
- *trans*-1,4-polybutadiene
  - A is not of the lowest energy, B is.
  - 4 **U**'s
  - $\mathbf{U}_1 = 1$
  - $\mathbf{U}_2 = [1\ \alpha\ 1] \sim [60^\circ\ 180^\circ\ {-60}^\circ]$
    - » $.5 < \alpha < 1$
  - $\mathbf{U}_3$, $\mathbf{U}_4 \sim 3 \times 3$
    - ≈ $\sigma > .5$ (CH---CH)
- *trans*-1,4-polyisoprene
  - similar to PBD
  - $\mathbf{U}_2 = [1\ 0\ 1] \sim [60^\circ\ 180^\circ\ {-60}^\circ]$
- comparing PBD and PIP
  - C_∞(PBD) ~ 5.8 < C_∞(PIP) ~ 7.4
  - TC(PBD) ~ -6E-4 > TC(PIP) ~ -3E-4

A

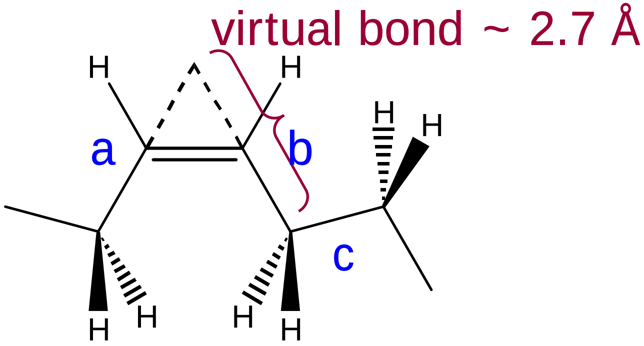


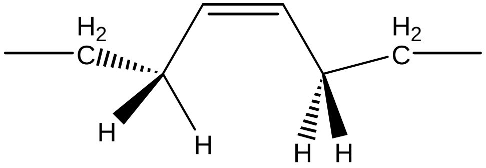
B

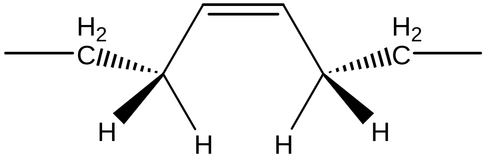




- ❑ *cis*-1,4-polybutadiene
  - 3 **U**'s
  - $\mathbf{U}_a$ = [1 1 1] ~ [0 60° -60°]
  - $\mathbf{U}_b = \begin{bmatrix} 0 & \zeta & \zeta \\ \zeta & 1 & 1 \\ \zeta & 1 & 1 \end{bmatrix}$
  - $\mathbf{U}_c$ = [1 σ σ]



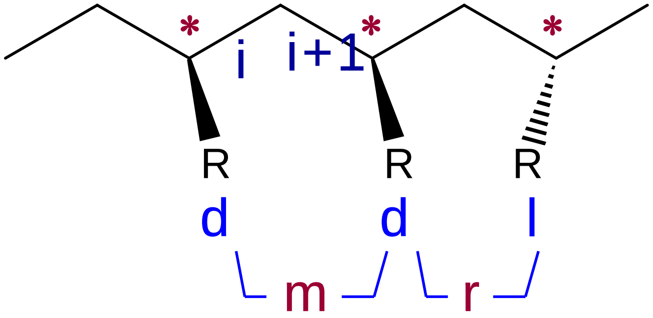




- ❑ comparing trans- and cis-PBD
  - C_∞(trans) ~ 5.8 > C_∞(cis) ~ 4.9
    - » small difference due to no cis conf for cis-PBD
  - TC(PBD) ~ -6E-4 < TC(cis) ~ +4E-4

Vinyl polymers

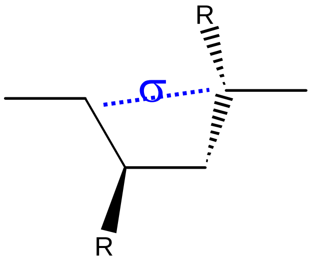
- asymmetric
  - due to chiral centers
  - G and G' with different popularity
    → different interactions
  - bond lengths the same
  - bond angle can be different

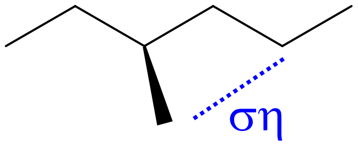


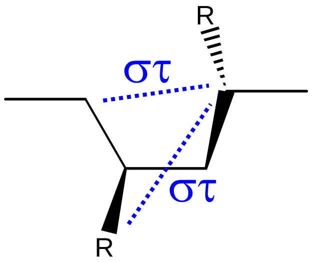
- 6 stat wt's per repeat unit ← 2 types of bond
  - » $CHR\text{-}CH_2$ ~ i ~ ϕ'
  - » $CH_2\text{-}CHR$ ~ i+1 ~ ϕ''

1st-order interaction

- d - i
  - σ for G (CH_2---CH)
  - $\sigma\eta$ for T
    - » if R(R) > R(CH_2) → $\eta < 1$
      - like Ph
    - » if R(R) ~ R(CH_2) → $\eta \sim 1$
      - like alkyl
  - $\sigma\tau$ for G'
    - ≈ $\tau < \sigma < 1$ ($\tau \sim .1 - .4$) ← two-way interaction
  - $\mathbf{D}_d' = \begin{bmatrix} \eta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \tau \end{bmatrix}$

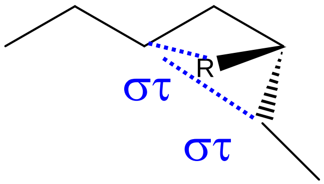






1st-order interaction

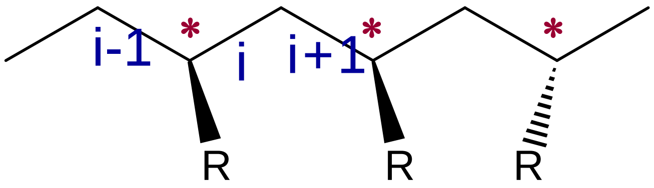
- d - i+1
  - στ for G
  - ση for T
  - σ for G'
  - $\mathbf{D}_d'' = \begin{bmatrix} \eta & 0 & 0 \\ 0 & \tau & 0 \\ 0 & 0 & 1 \end{bmatrix}$



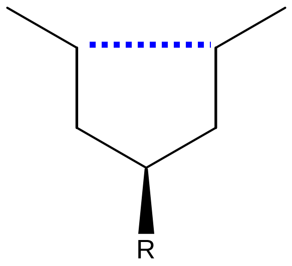
- l - i $\qquad \mathbf{D}_l' = \begin{bmatrix} \eta & 0 & 0 \\ 0 & \tau & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{D}_d''$

- l – i+1 $\qquad \mathbf{D}_l'' = \begin{bmatrix} \eta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \tau \end{bmatrix} = \mathbf{D}_d'$

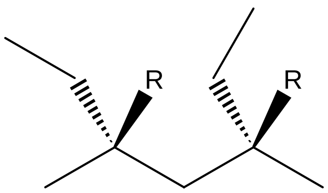
2nd-order interaction



- i-1 & i
  - the same to PE (CH_2---CH_2)
  - $\mathbf{V}_d' = \mathbf{V}_l' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & \psi & \omega \\ 1 & \omega & \psi \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix}$

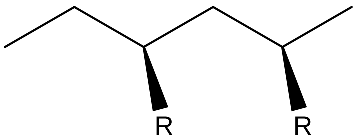


- i & i+1
  - CH_2---CH_2, CH_2---R, R---R
  - let all stat wt's be ω (ω ~ 0)
  - $\mathbf{V}_{dd}'' = \begin{bmatrix} \omega & \omega & 1 \\ 1 & \omega & \omega \\ \omega & \omega^2 & \omega \end{bmatrix}$

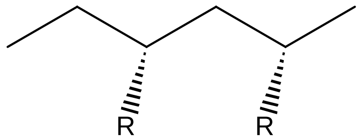


2nd-order interaction

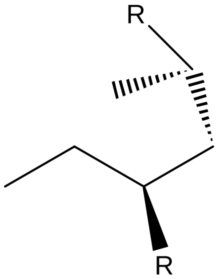
- $\mathbf{V}_{ll}$”, $\mathbf{V}_{ld}$”, $\mathbf{V}_{dl}$”
  - obtained by permutation of G and G’



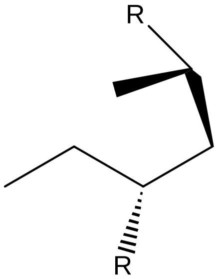
TT($\mathbf{V}_{dd}$”)



TT($\mathbf{V}_{ll}$”)



GG($\mathbf{V}_{dd}$”)



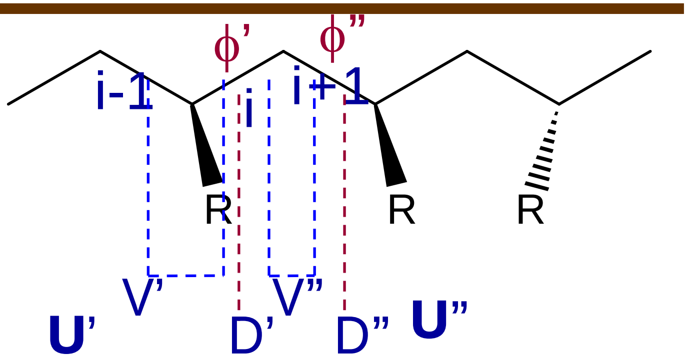
G’G’($\mathbf{V}_{ll}$”)

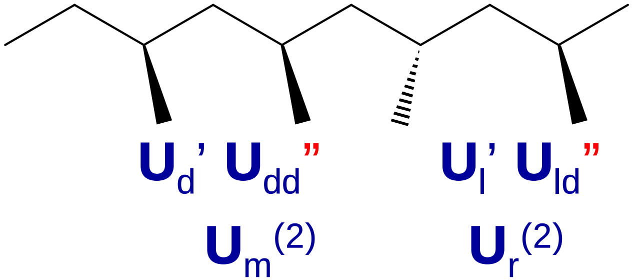
- ω
  - $\omega \sim 0$
  - for PVC, R(Cl)<R(CH_2)
    - ≈ ω(Cl---Cl) > ω(CH_2---Cl) > 0
  - for PVA, R(OH)<R(CH_2)
    - ≈ ω(OH--OH) > 1
    - ≈ ω(CH_2---OH) > 0

Calculation

- 6 **U**'s
  - $\mathbf{U}_d' = \mathbf{V}' \mathbf{D}_d'$
  - $\mathbf{U}_{dd}'' = \mathbf{V}_{dd}'' \mathbf{D}_d''$
  - $\mathbf{U}_{dl}'' = \mathbf{V}_{dl}'' \mathbf{D}_l''$

    permutation of G and G'
  - $\mathbf{U}_{ld}'' = \mathbf{V}_{ld}'' \mathbf{D}_d''$





- partition function, Z
  - $Z = \mathbf{J}^* [\Pi\, \mathbf{U}_i]\, \mathbf{J}$ (for i from 2 to n-1)

    $= \mathbf{J}^* [\Pi\, \mathbf{U}_i' \mathbf{U}_{i+1}'']\, \mathbf{J}$ (for i/2 from 1 to x-1, x=n/2)

    $= \mathbf{J}^* [\Pi\, \mathbf{U}_k^{(2)}]\, \mathbf{J}$ (for k from 1 to x-1, x=n/2)

    $\mathbf{U}_k^{(2)} = \mathbf{U}_m^{(2)}$ or $\mathbf{U}_r^{(2)}$

- chain dimension
  - $\langle r^2 \rangle_0 = 2 Z^{-1} \mathcal{J}^* \mathbf{G}_1 (\mathbf{G}_k^{(2)})^{x-1} \mathbf{G}_n \mathcal{J}$

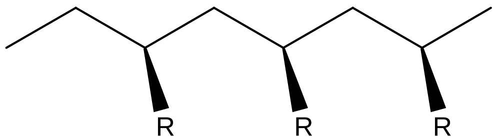
Preferred conformation

- $\omega<1$, $\tau\omega<1$, $\eta\sim1$

$$U_{dd}'' = \begin{bmatrix} \eta\omega & \tau\omega & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & 0 & \omega \end{bmatrix}$$

$$U_d' = \begin{bmatrix} \eta\tau^* & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{bmatrix}$$

  - dd

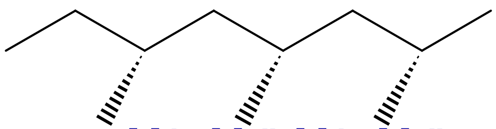


U_d' U_{dd}'' U_d' U_{dd}''

T G' T G' ~ left-handed

G T G T ~ right-handd

  - ll



U_l' U_{ll}'' U_i' U_{ii}''

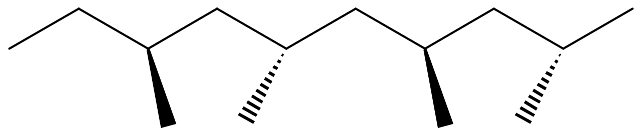
T G T G ~ right-handed

G' T G' T ~ left-handd

✓ isotactic ~ all left or right handed

Preferred conformation

- dl, ld



U_d'	U_{dl}''	U_l'	U_{ld}''	U_d'	
T	T	G'	G'	T	η^2
G	G	T	T	G	η^2
	T	T	T	T	$\eta^4\tau^{*2}$

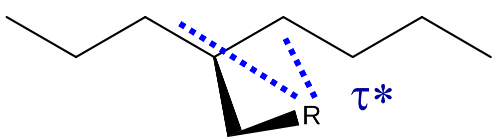
$$U_{dl}'' = \begin{bmatrix} \eta & \omega & \tau\omega \\ \eta\omega & 1 & \tau\omega \\ \eta\omega & \omega & 0 \end{bmatrix}$$

$$U_l' = \begin{bmatrix} \eta\tau^* & \tau & 1 \\ \eta & \tau & \omega \\ \eta & \tau\omega & 1 \end{bmatrix}$$

$$U_{ld}'' = \begin{bmatrix} \eta & \tau\omega & \omega \\ \eta\omega & 0 & \omega \\ \eta\omega & \tau\omega & 1 \end{bmatrix}$$

$$U_d' = \begin{bmatrix} \eta\tau^* & 1 & \tau \\ \eta & \tau & \tau\omega \\ \eta & \omega & \tau \end{bmatrix}$$

✓ syndiotactic
  - » TTGG preferred
  - » TTTT less preferred (dep on τ^*)



stereo-regular and irregular chains

- stereoregular chains
  - isotactic ~ succession of $G_m^{(2)}$
  - syndiotactic ~ succession of $G_r^{(2)}$
- stereoirregular chains
  - mixture of m and r ~ random not block
    - » total of x-1 pairs with x-y-1 meso and y racemic
    - » Not $[G_m^{(2)}]$x-y-1 $[G_r^{(2)}]$y
  - Monte-Carlo simulation
    - ≈ ρ(iso) ~ probability of iso (d-d or l-l)
    - » generating x-1 random numbers between 0 and 1
      - ◆ number < ρ(iso) ~ iso dyad ~ $G_m^{(2)}$
      - ◆ number > ρ(iso) ~ iso dyad ~ $G_r^{(2)}$
    - » calculate dimension
    - » repeat