3.034 – Problem set #1 - solution

1) You were given a GPC curve showing a plot of the retention volume V_r (x-axis) versus height above baseline (y-axis) and told that the y-axis height values (usually from a UV or refractive index detector) are proportional to n_iM_i. In addition, calibration data were provided that made it possible to convert the retention volume numbers to values of M_i. Using the equations for M_n, M_w and PDI shown below, the below indicated values were calculated. Note, these numbers will vary a bit depending on how you "cut-up" the curve into select data points and how you estimated the values of H_i. A calibration plot of log M versus retention volume is attched to this Pset. Such a plot should be linear to be of value as a calibration curve.

M_n = 10,351 g/mole, M_w = 17,915 g/mole and PDI =1.7

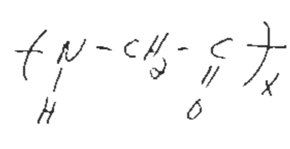
let $H_i = k\, n_i M_i$ (k → constant), thus $n_i M_i = \frac{H_i}{k}$ and $n_i = \frac{H_i}{k_i M_i}$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum \frac{H_i}{k}}{\sum \frac{H_i}{k M_i}} = \frac{\sum H_i}{\sum \frac{H_i}{M_i}}$$

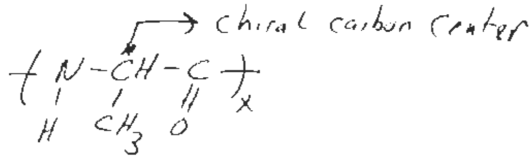
$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \sum w_{f_i} M_i = \sum \left(\frac{H_i}{\sum H_i}\right) M_i$$

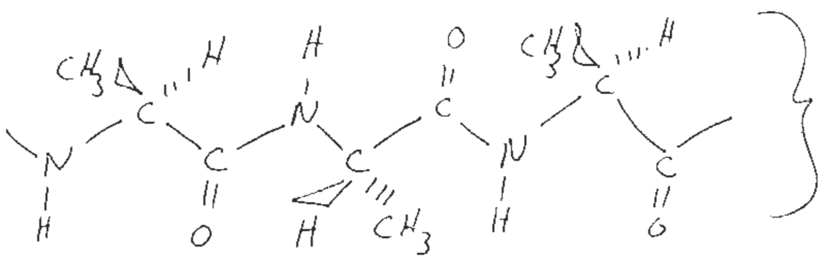
$$w_{f_i} = \frac{n_i M_i}{\sum n_i M_i} = \frac{H_i/k}{\sum H_i/k} = \frac{H_i}{\sum H_i}$$

2) The types of stereoisomers under consideration are cis/trans geometric isomers (different arrangement of atoms about a double bond) and/or polymer optical isomers (called tacticity- different arrangement of atoms about –CHR- groups as they appear along a polymer backbone). The ability to rotate the plane of polarized light, optical activity, is only possible when a polymer chain contains true chiral carbon centers (sp^3 hybridized carbons with 4 different bonds) and the chiral carbon centers are all the same mirror image type (ie., not present as a racemic mixture of mirror image isomers).

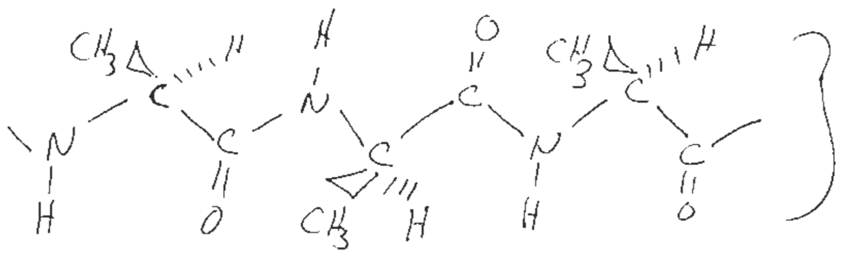


This polymer does not have any Stereoisomers, nor can it be optically active; no double bonds, no $-\overset{R}{\underset{H}{C}}-$ groups, no chiral carbon centers





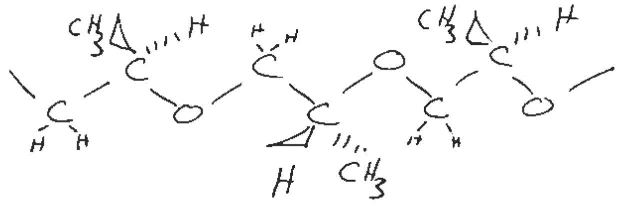
isotactic, optically active



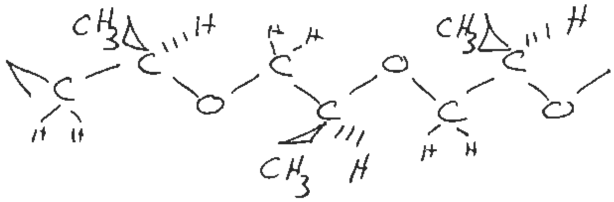
Syndiotactic isomer, no optical activity

Note: the synthesis of the syndiotactic polymer is not possible by normal means (to be discussed)

$-\!\!\left(CH_2-\overset{*}{C}H(CH_3)-O\right)\!\!-$ → chiral carbon center

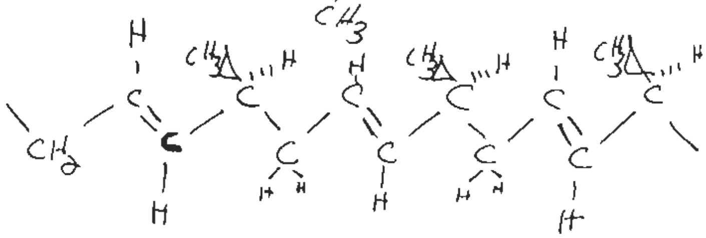


} isotactic, optically active

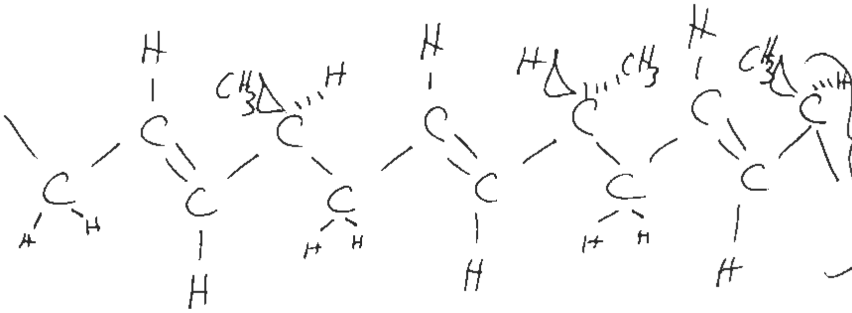


} Syndiotactic not optically active

$-\!\!\left(CH_2-CH=CH-\overset{*}{C}H(CH_3)\right)\!\!-_x$ → chiral carbon center

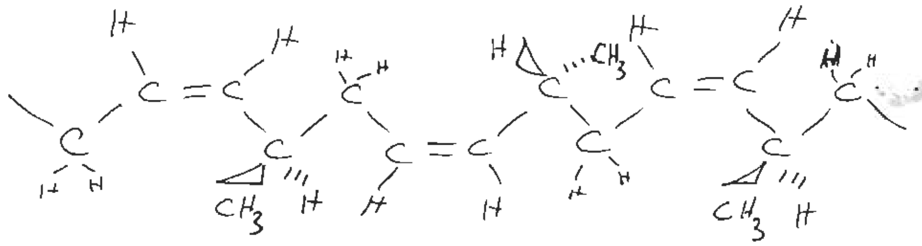


} trans-isotactic, optically active

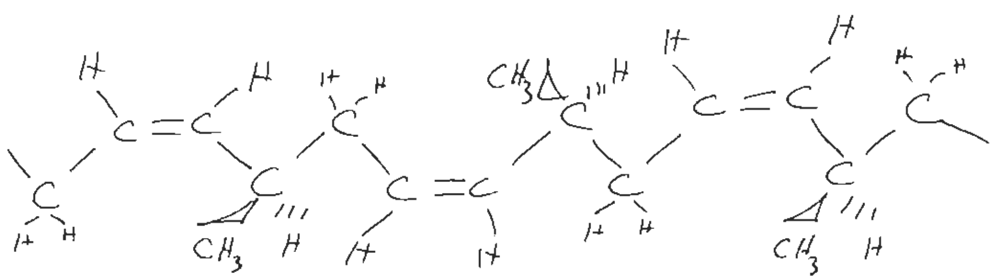


} trans-Syndiotactic, not optically active

$$\left(CH_2-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}} \right)_n$$

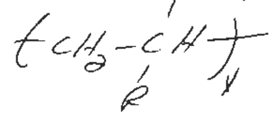


cis – isotactic, optically active



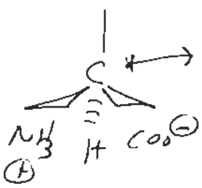
cis – Syndiotactic, not optically active

(2a)

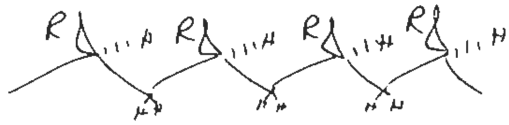


→ not a chiral carbon center

R =



↔ chiral carbon center



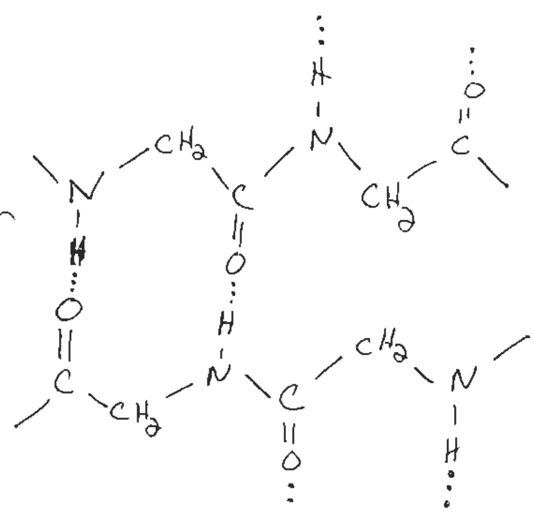
isotactic

Syndiotactic

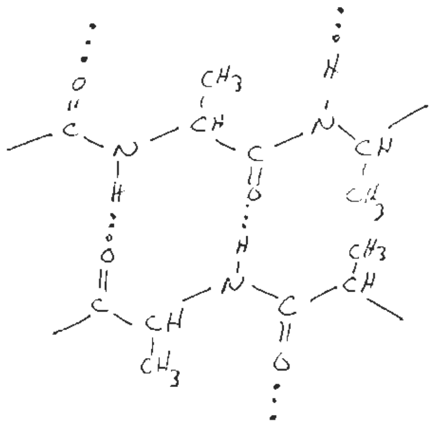
↑ Since this is the only mirror image isomer on the chain, all optical isomers of the polymer will be optically active. The optical activity comes from the side group!!

(2b)

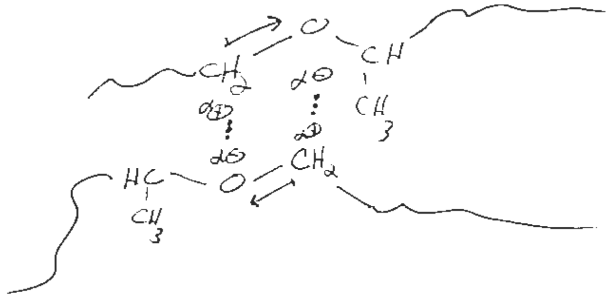
H-bonds



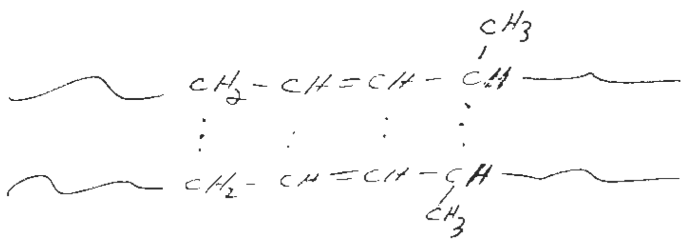
(2b)



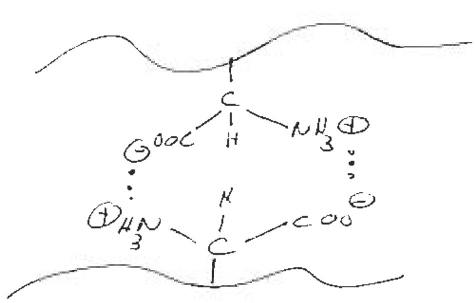
H - bonds



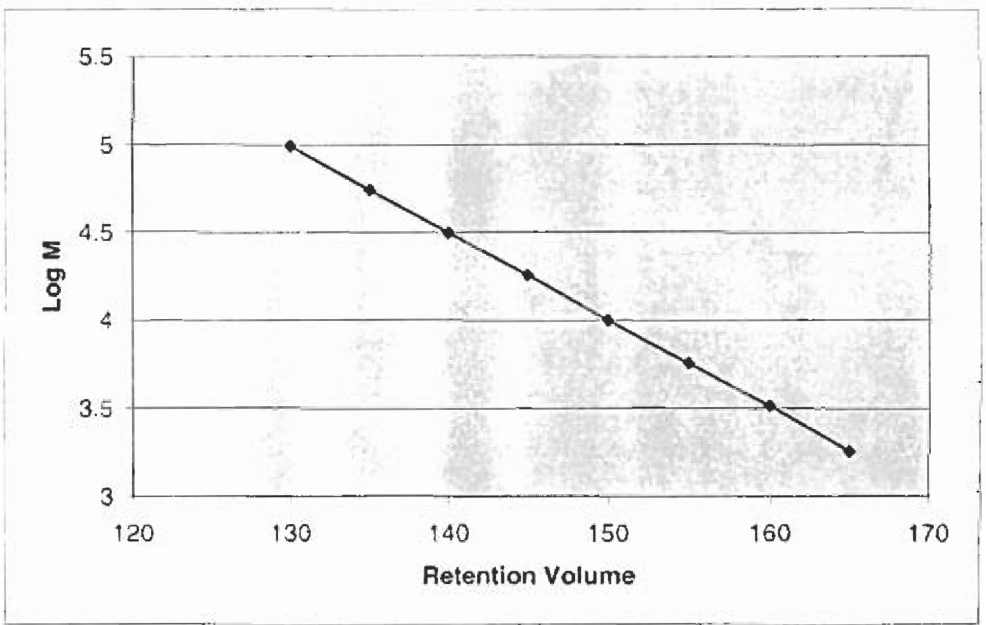
dipole-dipole



Van der Waals



ionic


5.5
5
4.5
4
3.5
3
Log M
120
130
140
150
160
170
Retention Volume