Polymer Basics & Molecular Weight

Polymer Characteristics

❖ **Can be describe by:**

❑ Microstructure
- **Organization of atoms along the chain that is fixed during the polymerization process**

❑ Architecture
- **Linear, ring, branched, ….**

❑ Degree of polymerization

However, a single flexible macromolecule can adopt many different conformations: Spatial structure which determine the relative locations of its monomers

- **Conformation that polymer adopt depends on three characteristics**

Flexibility of chains

Interaction b/w monomer on the chains (attractive or repulsive interaction)

Interaction with Surroundings

Some chains are stiff like piano & some quite flexible like a silk thread

Illustration:
Magnitude of variation in chain dimensions

- ❑ Consider a chain of $n=10^{10}$ bonds   Size of the bond: Å
- ❑ If we magnify all the lengths by 10^8 Size= l =1 cm
- ❑ Strong attraction b/w monomers
  - – Conformation of the polymer is a dense object   (Collapsed globule)

$$V \approx nl^3 \approx 10^{10} \text{ cm}^3 \approx 10^4 \text{ m}^3$$
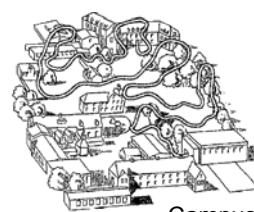$$R \approx V^{1/3} \approx n^{1/3}l \approx 20 \text{ m}$$

Room

- ❑ If there is no interaction between monomers
  - – Chain conformation is a random walk with size
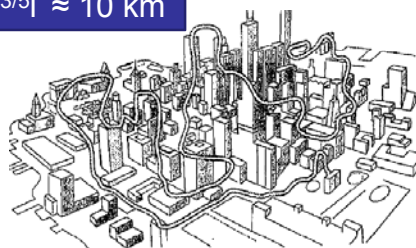
$$R \approx n^{1/2}l \approx 1 \text{ km}$$

Campus

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Illustration:
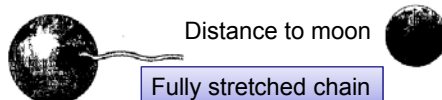## Magnitude of variation in chain dimensions

- ❑ Conformation of polymer with excluded volume repulsion
  - – Self avoiding walk with $R \approx n^{3/5}l \approx 10 \text{ km}$

City

- ❑ Conformation with long range repulsions
  - – Adopt an extended conformation with size $R \approx nl \approx 10^5 \text{ km}$

Distance to moon

Fully stretched chain

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Polymer Liquids

❖Polymer solution or Polymer melt

- **Concentration of polymer can also explain by volume fraction of polymer**
    - (= ratio of occupied volume of the polymer and the volume of solution)

$$\phi = \frac{c}{\rho} = c\frac{v_{mon}\mathcal{N}_{Av}}{M_{mon}} \qquad \rho = \frac{M_{mon}}{v_{mon}\mathcal{N}_{Av}}$$

- ❑ Pervaded volume: volume of solution spanned by the polymer chain $\quad V \approx R^3$

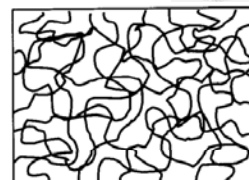- ❑ Overlap volume fraction (ϕ^*):volume fraction of a single molecule inside its pervaded volume

$$\phi^* = \frac{Nv_{mon}}{V} \qquad c^* = \frac{\rho Nv_{mon}}{V}$$
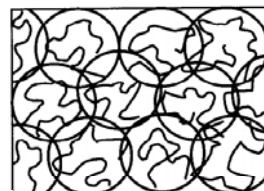
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Overlap Parameter (*P*):

Average number of chains in a pervaded volume that is randomly placed in the solution
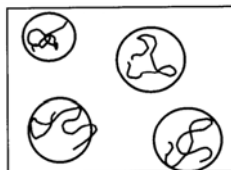
$$P = \frac{\phi V}{Nv_{mon}}$$

For polymer melt: $P \gg 1$

Semidilute ($\phi > \phi^*$)

Overlap ($\phi = \phi^*$)
$$P \cong 1$$

Dilute ($\phi < \phi^*$)

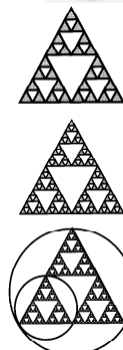**Polymer Science & Technology (CL-623)**

1/18/2012

Fractal Nature of Polymer conformation
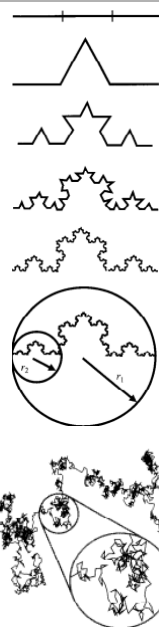
Fractal: Self similar over a wide range of length scale

Fractal dimension of any polymer is defined through the relation b/w number of monomer in any section of polymer and root mean square size.

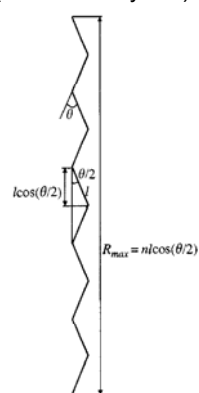$$g \sim \left(\sqrt{\langle r^2 \rangle}\right)^{D}$$

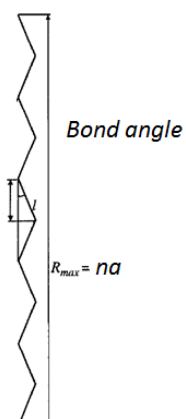| Architecture	Interactions	Space dimension d	$\mathcal{D}$
Linear	None	Any	2
Linear	Short-range repulsion	$d=2$	4/3
Linear	Short-range repulsion	$d=3$	1.7
Randomly branched	None	Any	4
Randomly branched	Short-range repulsion	$d=2$	8/5
Randomly branched	Short-range repulsion	$d=3$	2.0
Incipient gel	Partially screened repulsion	$d=2$	91/48
Incipient gel	Partially screened repulsion	$d=3$	2.5

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Constitution of Polymer chain

Contour length (Rod like Polymer) Fully stretched chain Collapsed globule state (coiled)

$l\cos(\theta/2)$

$R_{max} = nl\cos(\theta/2)$

Bond angle

$R_{max} = na$
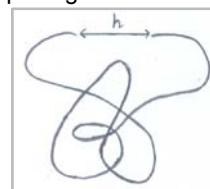
Freely jointed chain
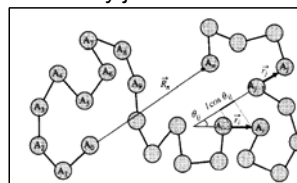
Kuhn length   End to end vector $\vec{R}_n = \sum_{i=1}^{n} \vec{r}_i.$

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4

Average radius area and volume of polymer

$$\bar{r} = \frac{1}{5}\sum r_i \qquad A_i = 4\Pi r_i^{\,2} \qquad \sum 4\Pi r_i^{\,2} = A_{total}$$

$$r_i = \left(\frac{A_i}{4\Pi}\right)^{\frac{1}{2}} \qquad <A> = \frac{4\Pi}{5}\sum r_i^{\,2} \qquad r_g^{\,2} = \frac{\sum_i n_i r_i}{\sum_i m_i}$$

$$<r_i> = \frac{3}{4}(V_i)^{\frac{1}{3}}$$

$$V_t = \frac{4}{3}\Pi\sum r_i^{\,3} \qquad <r_i> = \left(\frac{<A>}{4\Pi}\right)^{\frac{1}{2}} \qquad r_g^{\,2} = \frac{\int r^2 dm}{\int dm}$$
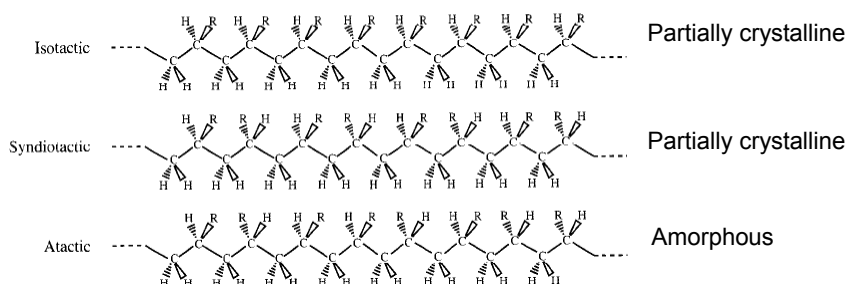
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Conformational/ configurational Isomerism

❖ **configurational Isomerism**

  ▪ **Spatial arrangement of substituent groups**

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❖ Butane Molecule

gauche *cis* *gauche* *trans*
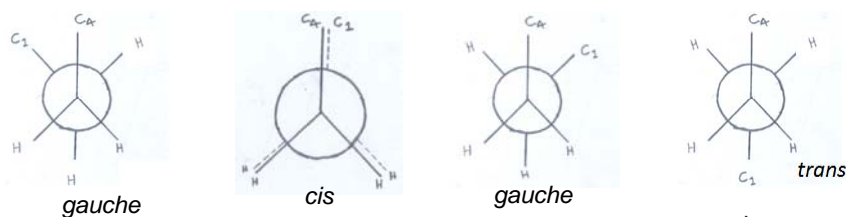
❖ Polymer backbone

Torsion angles

$trans\ \varphi_i = 0°$ $gauche_+\ \varphi_i = 120°$

$\Delta\varepsilon$ determines the relative probability of a torsion angle being in a gauche state in thermal equilibrium
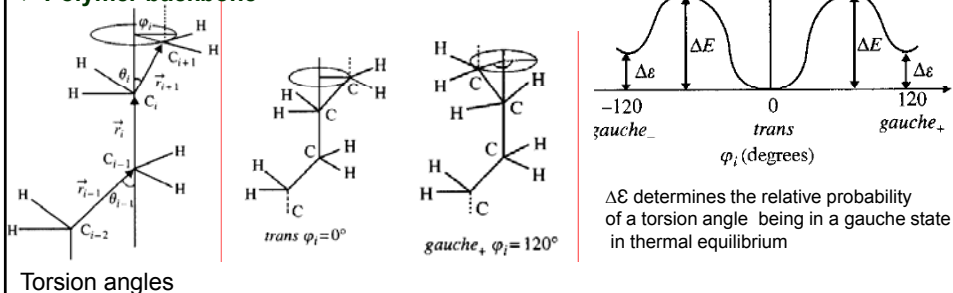
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Relative Energy of Butane conformations

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Geometrical Isomerism

❖ **If polymer chains have π bonded sites along the polymer chains**

❑ Structure can appear in many isomeric state

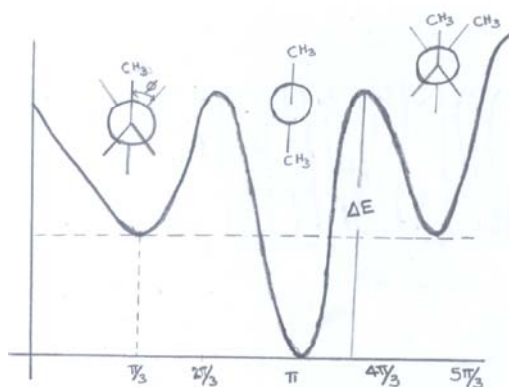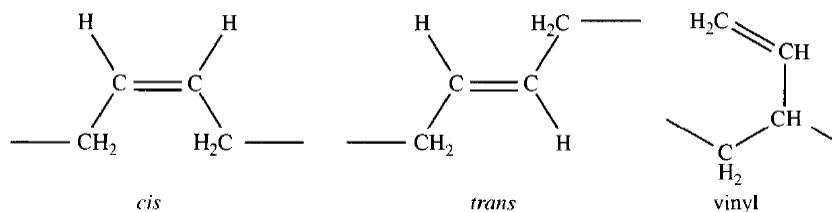*cis*   *trans*   *vinyl*

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Molar Mass and Degree of Polymerization

❑ Properties of polymerization $\alpha f(M)$

α (size of chains)

Molar mass
gm/mol
Kg/mol
Dalton

Molar mass of homopolymer is related to degree of polymerization

Molar mass of repeat units $M = xM_\circ$

$$\sum f_i M_j$$

f_j=Chain fraction of containing monomer

Molar mass for copolymer having repeat unit A and B

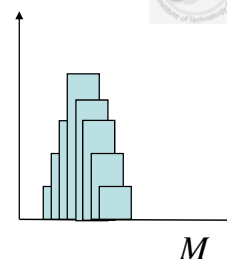$$M = x_A M_{A_\circ} + x_B M_{B_\circ} = \sum_{i=1}^{n} x_i M_{i_\circ}$$

M of polymer incorporate the distribution of chain lengths of polymer

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Molecular Weight of Polymer

Average molecular weight (**M**)

$$\overline{M} = \frac{\sum x_i M_i^{\alpha}}{\sum x_i M_i^{\alpha-1}}$$

Number average molecular weight (**M$_n$**)

$$\overline{M_n} = \sum x_i M_i = \frac{\sum\limits_{i=1}^{\infty} M_i N_i}{\sum\limits_{i=1}^{\infty} N_i}$$

Weight average molecular weight (**M$_w$**)

$$\overline{M_W} = \sum\limits_{i=1}^{\infty} W_i M_i$$

The sum of the products of the molar mass of each Fraction Multiplied by its weight fraction

$$W_i = \frac{N_i M_i}{\sum N_i M_i}$$

$$= \frac{1}{\sum x_i M_i}(\sum x_i M_i) M_i$$

$$\overline{M_W} = \frac{\sum x_i M_i^2}{\sum x_i M_i}$$

$$\overline{M_n} = \frac{\sum W_i}{\sum (W_i / M_i)}$$

M_i

x_i

x_i

M

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$M_n = M_w$ For perfectly monodisperse polymer

$M_W > M_n$ Other than monodisperse polymer

❑ Certain method of molar mass measurement such as sedimentation equilibrium yields the Z average molar mass (M_Z)

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum W_i M_i^2}{\sum W_i M_i}$$ $$\overline{M_Z} > \overline{M_W} > \overline{M_n}$$
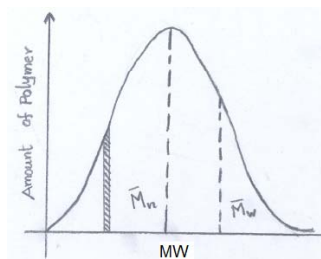
PDI:-is useful measure of the breath of the molecular weight distribution curve (Polydispersity or heterogeneity Index)

Number average degree of polymerization $x_n = \dfrac{M_n}{M_o}$

Weight average degree of polymerization $x_w = \dfrac{M_w}{M_o}$

$$\overline{Dp_i} = \frac{\overline{M_n}}{M_o}$$

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Estimate DP$_n$ and PDI of PVC

MW range	x_i
5-10K	0.05
10-15K	0.16
15-20K	0.22
20-25K	0.27
25-30K	0.20
30-35K	0.08
35-40K	0.02
Total	

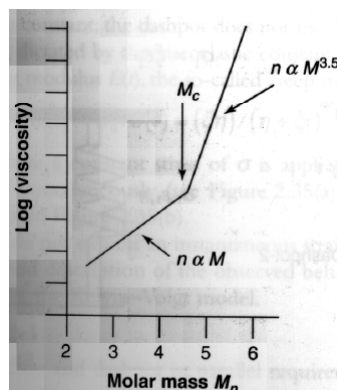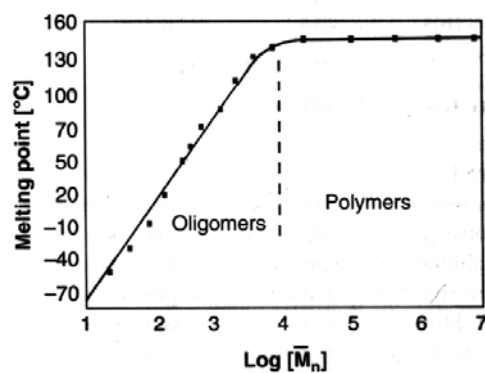| Mean	x_iM_i	w_i	w_iM_i
7500	375	0.0177	150
12500	2000	0.094	1250
17500	3850	0.18	3150
22500	6075	0.29	6525
27500	5500	0.26	7150
32500	2600	0.123	4225
37500	750	0.035	750
	21150	1.00	23200

DP$_n$=21150/62.5= 338.4

PDI=23200/21150=1.09

❑ A polystyrene contains: 1g of 10000 Da, 2g of 50,000 or 2 gm of 100000Da. Calculate Mn, Mw and PDI of the mixture?

$$\overline{M}_n = \frac{\sum W_i}{\sum (W_i / M_i)}$$

❖ **Molecular weight Dependence**

Molar Mass Measurement Techniques

Method	Absolute	Relative	M_n	M_w	A_2	Range ($g\,mol^{-1}$)
End group analysis	×		×			$M_n < 10\,000$
Vapor pressure osmometry	×		×		×	$M_n < 30\,000$
Cryoscopy	×		×		×	$M_n < 30\,000$
Ebulliometry	×		×		×	$M_n < 30\,000$
Membrane osmometry	×		×		×	$20\,000 < M_n$
Light scattering (LS)	×			×	×	$10^4 < M_w < 10^7$
Intrinsic viscosity (IV)		×				$M < 10^6$
SEC[a] with c detector		×	×	×		$10^3 < M < 10^7$
SEC[a] with c and LS detectors	×			×		$10^4 < M < 10^7$
SEC[a] with c and IV detectors		×	×	×		$10^3 < M < 10^6$
MALDI-TOF-MS[b]	×		×	×		$M < 10\,000$

Size Exclusion Chromatography
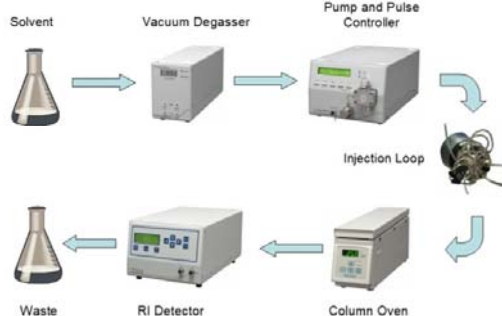
❑ Also Known as Gel Permeation Chromatography
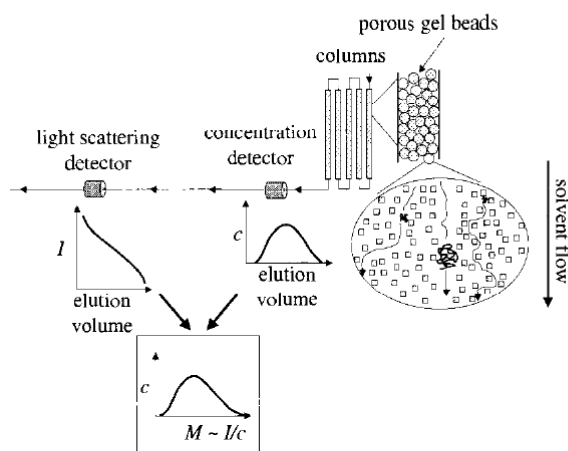
Pervaded volume of the coil: The volume within the columns that is accessible to a polymer determines how long the polymer can stay in the column

SEC Analysis: Instrument

❖ **Detectors**

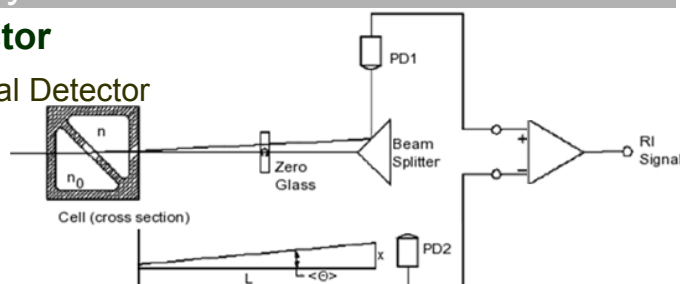❑ RI Detector:

❑ UV Detector:

❑ LS Detector:

❑ IV Detector:

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SEC Analysis

❖ RI Detector

❑ Universal Detector
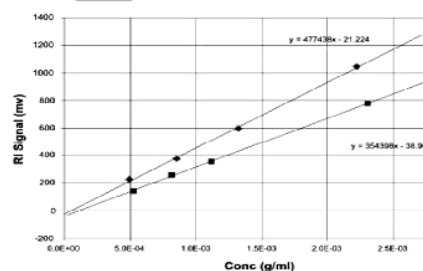

$$RI.signal = RI.Cal \cdot \frac{n - n_0}{n_0}$$

$$\frac{dn}{dc} = \frac{n - n_0}{C}$$

$$RI.Signal = \frac{RI.Cal}{n_0} \cdot C \cdot \frac{dn}{dc}$$

$$RI_i = \frac{RI.Cal}{n_0} \cdot \frac{dn}{dc} \cdot C_i$$

$$\Delta V = \frac{\Delta t \cdot Q}{60}$$

$$RI.Area = \Delta V \sum_i RI_i = \frac{RI.Cal}{n_0} \cdot \frac{dn}{dc} \cdot Conc.S \cdot V.inj$$

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Individual pore size GPC columns

Packing of column: styrene/divinylbenzene gel

Molecular weight range	Pore size
100 - 1000	50 Å
250 - 2500	100 Å
1,000 - 18,000	500 Å
5,000 - 40,000	10^3 Å
10,000 - 200,000	10^4 Å
50,000 - 1,000,000	10^5 Å
200,000 - > 5,000,000	10^6 Å
500,000 - ~20,000,000	10^7 Å
~1,000 - 10,000,000	Mixed Bed - High
~100 - 100,000	Mixed Bed - Low

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❑ Response from RI Detector with Retention volume
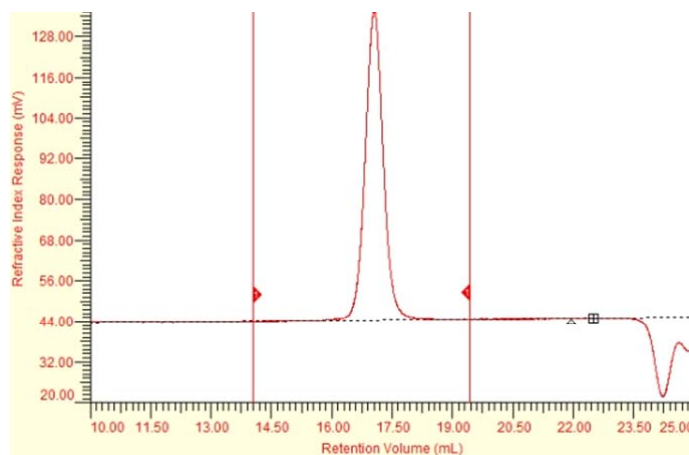
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Detector Calibration

$y = 35587x - 0.154$

$y = 24845x + 0.0461$

◆ PS (NIST 1478) ■ Polybutadiene

$$Slope = \frac{\Delta RI.Area}{\Delta Conc.S} = \frac{RI.Cal}{n_0} \cdot \frac{dn}{dc} \cdot V.inj$$

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❖ PS sample caliberation

$$\frac{dn}{dc} \geq 0.05 \ mLg^{-1}$$
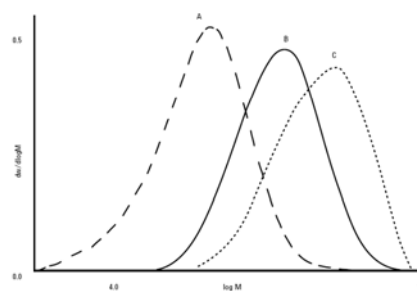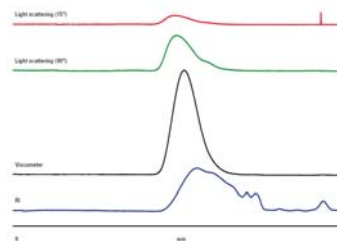
UV Detector

Beer-Lambert Law states

Absorbance A = constant x concentration x cell length
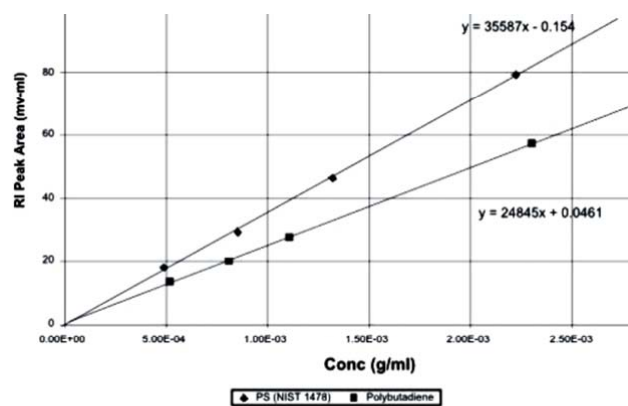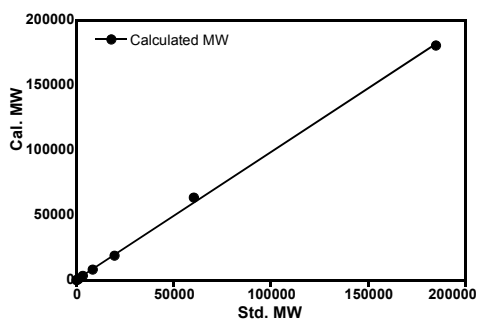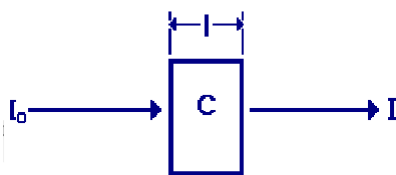

thickness (l)

concentration (C) of the solution

$A = \log_{10}(Io/I) = \log_{10}(100/T) = kcL$

L is the length of the radiation path through the sample

k extinction coefficient - a constant dependent only on the nature of the molecule and the wavelength of the radiation

❑ UV detector is excellent for:

– styrenic type polymers,

– (polystyrene, styrene/isoprene, styrene/butadiene, ABS, etc.), epoxies, phenolics, polycarbonates, polyurethanes, and aromatic polyesters

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UV Detector contd..

❑ By addition of photodiode array (PDA) detector
  – Can look at wide variety of wavelengths instantaneously
  – Allows us to determine something about the chemical composition distribution (copolymer sequence)

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Frictional properties of Polymer molecules

❖Fractional coefficients of polymer molecules in dilute solution–

  ❑ Two extremes of fractional behaviour of polymer molecules can be identified – namely free draining and non-draining

❖**Free draining polymer molecule**:-

when solvent molecules are able to flow past each segment (x) of the chain, are considered by dividing them into identical segments each of which has the same contribution towards fractional coefficient (ε)

$$f_o = x\,\varepsilon \quad x = number \quad of \quad sagments \quad in \; chain$$

f_0 : FC of a polymer molecule upon chain length

  ❑ Dominant in short chain molecule and for highly elongated rod like molecules.
 ❑ For flexible chains it decrease rapidly as the chain length increases

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Frictional properties of Polymer molecules contd..

❖ Non-draining **polymer molecule**

when solvent molecules within the coiled polymer chain move with it. A non-draining polymer molecule can represented by an equivalent impermeable hydro dynamic particle have same $f_o = 6\eta_o \pi R_H$ where $\eta_o = vis\cos ity\ of\ solvent\ R_H$
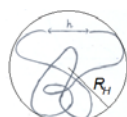
Impermeable hydrodynamic sphere

where $R_H \propto \left\langle h^2 \right\rangle^{1/2}$ $\quad \left\langle h^2 \right\rangle^{1/2} \propto x^{1/2}$ $\quad$ highly expanded coil

$$f_o = K_o \alpha_n \left\langle h^2 \right\rangle^{1/2} \qquad\qquad \left\langle h^2 \right\rangle^{1/2} \propto x^{1/10}$$

K_o =constant, α_n =expansion parameter for the hydrodynamic chain dimension

For small expansion $\quad \alpha_\eta = a_s^{0.81} \qquad a_s > a_\eta$

$$f_o = K_o'' x^{a_o} \qquad 0.5 \leq a_o \leq 0.6$$

Actually the frictional behaviour of real polymer comprises both type of draining contributions.

Hydrodynamic volume and intrinsic viscosity in the non-draining limits viscosity of a suspension of rigid non-interacting sphere is given by Einstein equation:

Dilute Solution Viscometry

Characteristic feature of a dilute polymer solution is that its viscosity is considerably higher than that of either pure solvent or dilute solution of small molecules.

Such measurement is used to determine molecular weight of a polymer.

❑ Intrinsic viscosity [η]

It relates to the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature.

$$\eta \propto \text{ Dimension of polymer molecule in solution}$$

Viscosity can provide the information on molecular shape, degree of polymerization, polymer solvent interaction,

Terminology used in dilute solution viscometry

Common name	Name proposed by IUPAC	Symbol and definition
Relative viscosity	Viscosity ratio	$\eta_r = \eta / \eta_0$
Specific viscosity	—	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \ln(\eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \lim_{c \to 0}(\eta_{red})$

$$\eta_{sp} = K_o[\eta]C + K_1[\eta]^2 C^2 + K_2[\eta]^3 C^3 + \ldots\ldots\ldots$$

$K_o, K_1, K_2\ldots\ldots$ dimensionless constant and $K_o=1$ for dilute solution

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2 C \qquad ----(1)$$

Huggins equation; valid for $[\eta]C \ll 1$

K_H =rang 0.3 (good polymer solvent pair)

= rang 0.5 (poor polymer solvent pairs)

K_H is independent of molar mass

For dilute solution ($\eta_{sp} \ll 1$)

$$\log(\eta_r) = \log(1 + \eta_{sp}) \cong \eta_{sp} - \frac{1}{2}\eta_{sp}^2 \qquad ----(2)$$

Put eq.1 into eq. (2)

$$\log(\eta_r) = [\eta]C + K_H[\eta]^2 C^2 - \frac{1}{2}\left[[\eta] + K_H[\eta]^2 C\right]^2 + [\eta]C + K_H[\eta]^2 C^2 - \frac{1}{2}\left[\eta^2 + K_H^2\eta^2 C^2 - 2\eta^3 K_H C\right]$$

$$\log(\eta_r) = [\eta]C + \left(K_H - \frac{1}{2}\right)[\eta]^2 C^2 + \ldots\ldots\ldots$$

$$\frac{\ln\eta_r}{C} = [\eta] + \left[K_H - \frac{1}{2}\right][\eta]^2 C$$

$K_K = \left(K_H - \frac{1}{2}\right)$ May be negative or zero

$$\frac{\ln\eta_r}{C} = [\eta] + K_K[\eta]^2 C \qquad \ldots.(3) \; C \ll 1 \; \text{Kraemer equation}$$

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Mark-Houwink equation $\qquad [\eta] = K\overline{Mv}^a$ $\qquad$ At infinite dilution

K tends to decrease as 'a' increases for flexible chains $\qquad K \cong 10^{-3} \, to \, 10^{-1} \, cm^3 \, g^{-1}$

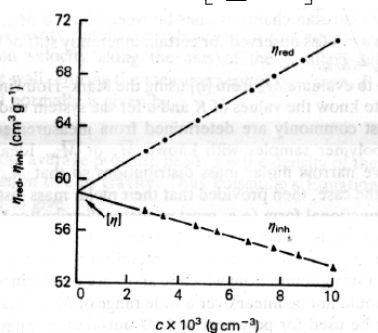$$\eta_{sp} = \sum(\eta_{sp})_i \qquad C_i = n_i M_i \qquad (\eta_{sp})_i = C_i[\eta]_i \qquad [\eta]_i = K M_i^a$$

$$[\eta] = \left[\eta_{sp}/C\right]_{C\to 0} = K\left[\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}\right] \qquad \overline{M}_v = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}\right)^{1/a}$$

For Gaussian chain $\overline{M}_v$ lies between $\overline{M}_n$ & $\overline{M}_w$

if a=1;

$$\overline{M}_v = \overline{M}_w$$

But a=0.7 polymer in good solvent

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Hydrodynamic volume & $[\eta]$ in non-draining limits

❖**Einstein equation:**

$$\eta = \eta_o \left[1 + \frac{5}{2}\phi_2 \right]$$

η viscosity of suspension
η_o viscosity of suspension medium
$\phi \rightarrow$ volume of sphere
[impermeable polymer coil of hydrodynamic volume V_n]

Suspension of rigid & non interacting sphere

M=molecular mass of polymer

$$\phi_2 = \left(\frac{c}{M} \right) N_A V_n$$

$$\eta_{sp} = \frac{(\eta - \eta_o)}{\eta_o}$$

$$\eta_{sp} = \left(\frac{5}{2} \right)\left(\frac{c}{M} \right) N_A V_n$$

$$[\eta] = \lim_{c \to 0} \left[\eta_{sp} / c \right]$$

$$[\eta] = \frac{5}{2}\frac{N_A V_h}{M}$$

$$V_h = \frac{2}{5}[\eta]M \Big/ N_A$$

$$V_h \propto \left(\alpha_n \langle S^2 \rangle^{1/2} \right)^3$$

$$[\eta] = \phi_o^{\ s} \alpha_n^{\ 3} \left(\frac{\langle S^2 \rangle^{3/2}}{M} \right)$$

$$\phi_o^{\ s} = 3.67 \times 10^{24} \ mol^{-1}$$

For non-draining $\phi_o^{\ s}$ is independent of chain structure and chain length depend on the distribution of segments in the molecular coils.

Flory-Fox equation:

$$[\eta] = K_\theta \, \alpha_n^{\ 3} M^{1/2} \quad K_\theta = \phi_o^{\ s} \left(\frac{\langle S^2 \rangle_o^{3/2}}{M} \right)$$

$$\alpha_n \propto x^{1/10} \propto M^{1/10}$$

$$[\eta] = K M^a$$

$$0.5 \le a \le 0.8$$

K & 'a' are constant for given system;
'a' changes with degree of expansion of the molecular coils from their unperturbed dimensions
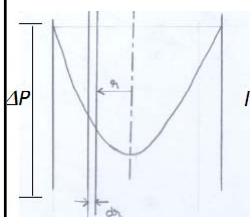A=0.5; under theta conditions

Relation is called as Mark-Houwink equation (based on experimental data)

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Measurement of solution viscosity

❖**Can be measured using capillary viscometer**

Under the condition of steady laminar Newtonian flow

Poiseuille's equation

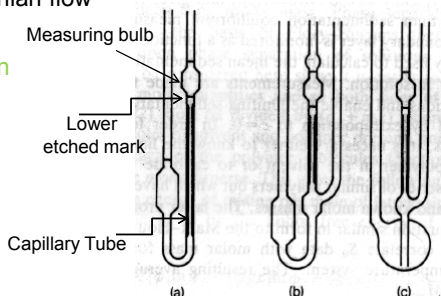$$\frac{V}{t} = \frac{\pi r^4 \Delta P}{8\eta l}$$

$$\frac{V}{t} = \frac{\pi r^4 \rho g \langle h \rangle}{8\eta l}$$

$$\eta = A\rho t$$

A is constant for given viscometer

Polymer solution of concentration c

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}$$

Measuring bulb

Lower etched mark

Capillary Tube

(a)   (b)   (c)

Ostwald U-tube viscometer

Ubbelohde viscometer

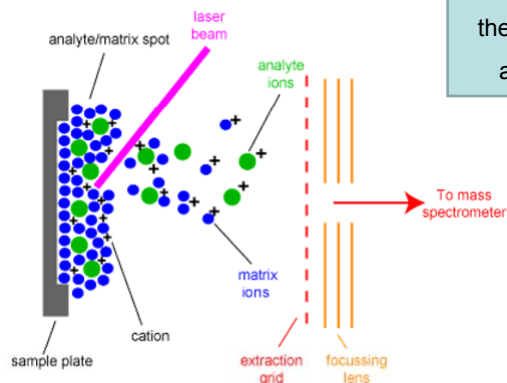Ubbelohde viscometer Large reservoir

Temperature control: ±0.01%

Flow time: ±0.1%

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MALDI-TOF-Mass Spectrometric Analysis

Principle:

laser beam is focused onto the surface of the matrix-analyte solid solution

Matrix-Assisted Laser Desorption/Ionisation (MALDI)-Time of Flight Mass spectrometry.

MALDI-TOF-Mass Spectrometric Analysis

Sample Preparation

MALDI-TOF MS instrument has been linearly calibrated with three standards Des-Arg 1, Bradykinn and Angiotensin-1 and ACTH (1-17).

The sample is prepared with an α- cyanohydroxy cinnamic acid (CHC) matrix (10mg/mL).

1 μL analyte solution (10mg/mL) is deposited onto the stainless steel sample plate, and allowed to air-dry.

Subsequently, a 1 μL matrix solution (50:50 v/v CHC: acetonitrile) is added into the analyte.

The differences between the measured and the calculated masses of peaks are matched within 0.5 D. We examine whether the peaks correspond to PLLA chains, bearing the catalyst as end group.
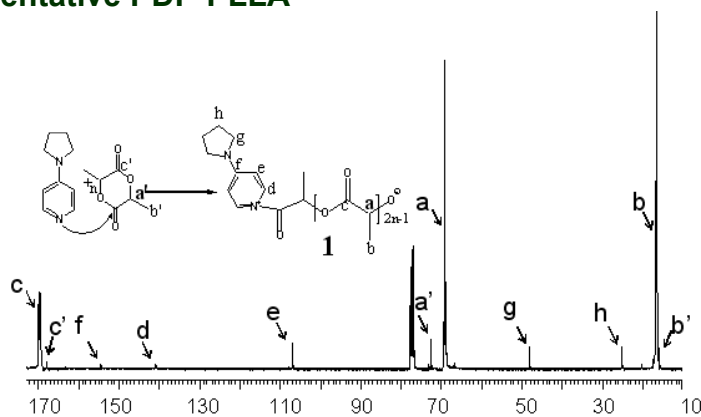
MALDI-TOF-MS spectra of PLA-NHC
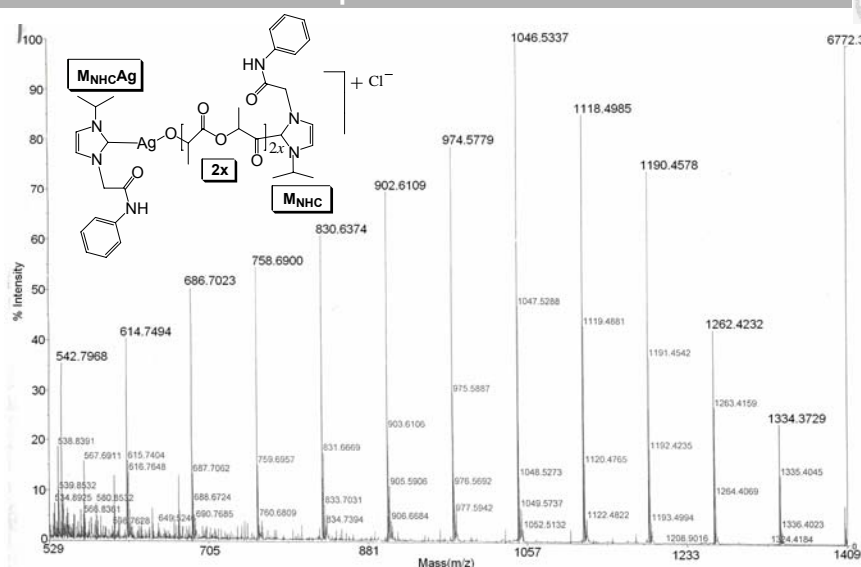
$M_c = 72x + M_{NHC}Ag + M_{NHC} + 23$

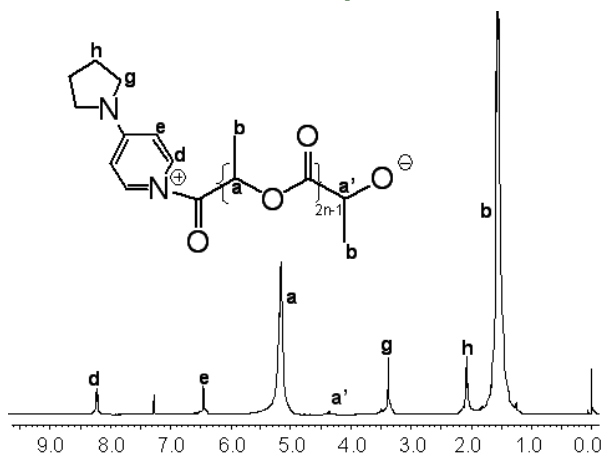=> PLA Chains End-Capped with Catalyst Fragments

^{13}C NMR Spectra
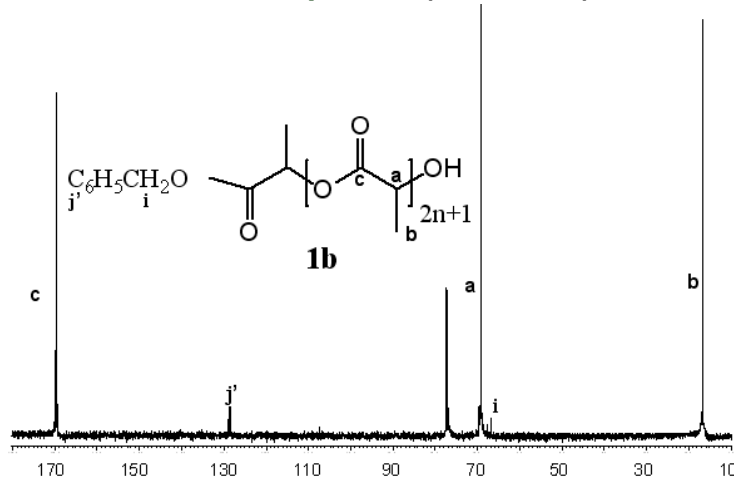
❖**Representative PDP-PLLA**

❖**Condition: [L/C=25] at 120°C for 90 min.**

❖α_{C-N} **peak shifted from 150 ppm. to 141 ppm.**

¹H NMR Spectra

❖**Representative PDP-PLLA samples**

❖**Condition: [L/C=25] at 120°C for 90 min.**

❖**¹H NMR spectrum (400 MHz) of PDP catalyzed PLLA in**

Mechanistic Studies cont'd..

❖**Representative ¹³C NMR Spectra: (PDP + BA)-PLLA**

❖**Benzyl Group present at the chain ends**

❖ References:

❑ Technical content from the following sources:

- Young R. J. & Lovell P.A. Introduction to Polymers, Champman & Hall 2nd Ed., reprinted 1994.
- M. Rubinstein and R. H. Colby, *Polymer physics*, Oxford University Press, USA, 2003
- J. R. Fried, *Polymer Science & Technology*, Prentice Hall of India, 2nd Ed., 2009.

Content from the books is included here exclusively for academic purpose.

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