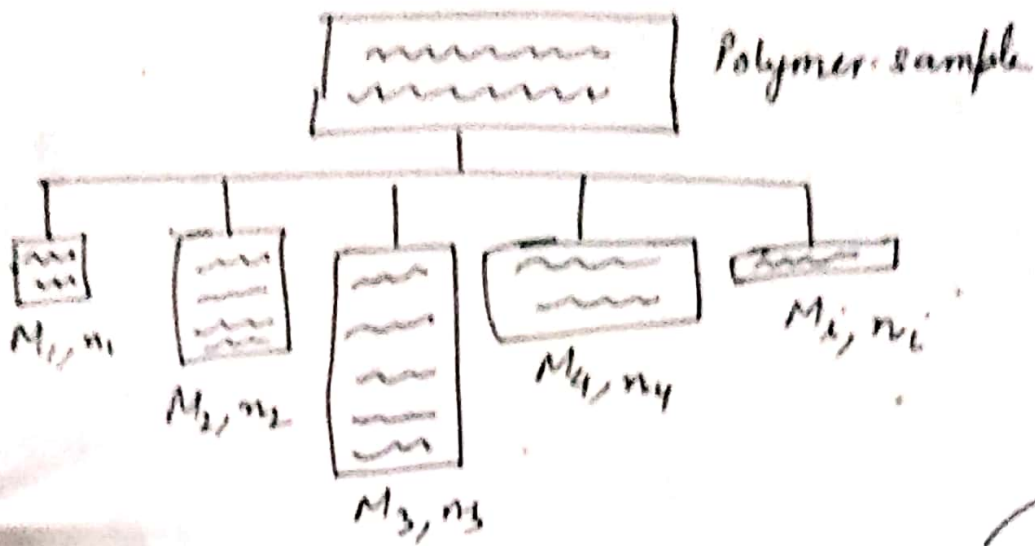


66
Polymer Sci
(Quantities)
Generalizations



$n = \text{number}$; $M = \text{molecular wt.}$

number avg
Mol. wt.
contribution
of its fraction

$$\sum n_i = n_1 + n_2 + n_3 + \dots + n_i$$

number average $\bar{M}_n = \frac{n_1 M_1 + \dots + n_i M_i}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i}$

weight avg. $\bar{M}_w = \frac{n_1 M_1^2 + \dots + n_i M_i^2}{\sum n_i M_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$

Viscosity avg Mol. wt.

Viscosity
average
molecular
wt.

$$\bar{M}_v = \left[\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{1/a}$$

a is a variable (its value ranging from 0.5 to 1)
in the Mark Houwink eqn which relates intrinsic
viscosity $[\eta]$ with \bar{M}_v .

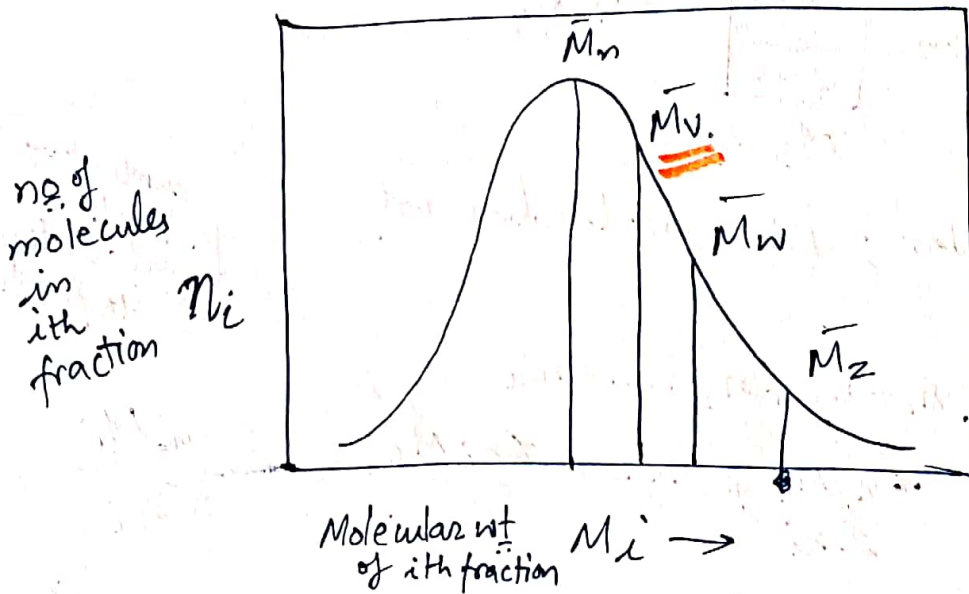
$n_i = \text{no. of molecules in } i\text{th fraction}$
 $M_i = \text{Molecular wt. of } i\text{th fraction.}$

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~~Experimental techniques used for
viscosity of dilute p.~~

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Goverilken



$\bar{M}_w > \bar{M}_n$

& \bar{M}_v is closer to \bar{M}_w than to \bar{M}_n

To know a polymer properly, we must have a knowledge of both the avg mol. wt as well as its dispersion pattern

12.6 Viscosity of dilute polymer solutions

The viscosity of dilute polymer solution depends on

- ① the nature of the polymer *linear, branched, etc*
- ② the nature of the solvent. *polar/non-polar, etc*
- ③ the concentration of the polymer
- ④ the concentration of the solvent
- ⑤ the polymer molecular weight
- ⑥ the temperature
- ⑦ the shear rate.

At the molecular level, the viscosity of a polymer solution is a direct measure of the hydrodynamic volume of the polymer molecules.

Hydrodynamic volume, is the apparent volume occupied by the expanded or swollen molecular coil along with the imbibed solvent and can be defined in terms of the expansion factor α and unperturbed end-to-end distance $\sqrt{\langle r_0^2 \rangle}$.

(Note 1, 2) P.T.O.

* α depends on the nature of the solvent

* $\sqrt{\langle \bar{r}_0 \rangle}$ depends on the molecular wt. of the polymer

" Therefore, a polymer will exhibit a higher viscosity in a good solvent than in a poor solvent and that in the same solvent, the viscosity will be directly proportional to the molecular ~~weight~~ weight. "

Note 1

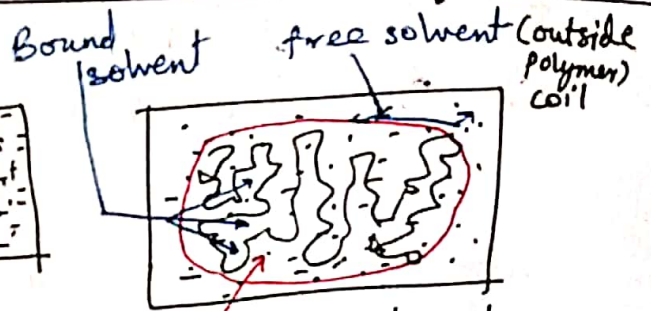
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solid polymer just added to solvent



Swollen Polymer in solvent.



Solvated polymer molecules diffusing out of the swollen mass.

Hydrodynamic volume
= volume ~~area~~ bound by red line

P. 77 Note 2

A real polymer ~~is~~ assumes different shapes over a period of time governed by random flight probability.

Since the bond angle of the actual polymer molecule is fixed, and there is less hindrance to free rotation, the unperturbed end to end distance will ~~be~~ always be higher than the root mean

square distance. $\sqrt{\langle \bar{r}_0 \rangle^2} = N l \sqrt{\langle \bar{r}_p \rangle^2}$

(random flight) (free joints, angles) \rightarrow flight

$\bar{r}_p = \text{r.m.s. distance (end to end)}$

$N =$ number whose value is > 1 . eg. PE = 2.6

$\bar{r}_0 =$ unperturbed dimension of the polymer molecule

$N \bar{r}_p^2 = \alpha^2 l^2 n$
 $l =$ Bond length $n =$ no. of bonds

12.6.1.
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Gron

Viscosity and molecular weight

Mark Houwink eqn.

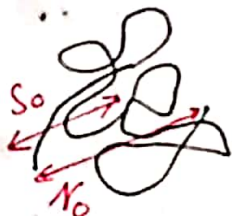
$$[\eta] = K \cdot \bar{M}^a$$

(38)

K and a are constants for a given polymer/solvent/temperature system. The value of a varies from 0.6 to 0.8 and becomes 0.5 in theta solutions solvents. Value of K varies (Note 3)

from one system to another.

(Note 3)
P 275



random coil
linear polymer
molecule



Branched molecule

S_0 = radius of gyration r_0 = end to end distance

- (A) Assume that the polymer molecule suspended in a solvent medium are free from interactive forces (i.e. no inter segmental $\left\{ \begin{array}{c} \text{C} \\ \text{C} \end{array} \right\} - \text{C} - \text{C} - \text{segment}$ attraction forces).
- (2) No solvent-segment interaction forces
- r_0 is the unperturbed dimension of the polymer chain;
or root mean square end to end distance
- $\sqrt{\langle r_0^2 \rangle} \propto l \sqrt{n}$ l = avg length of a segment
 n = no. of segments in the chain

(B) when we deal with branched polymers with same n & \bar{l} ; the main backbone length gets reduced. Some segments are utilized to form branches. This ~~causes~~ results in a lower r_0 , and more than two chain ends. Hence end to end distance cannot be spoken of. Hence use \downarrow
radius of gyration, \bar{S}_0 is the avg. distance between the molecular ~~ca~~ center of gravity & the chain ends.

$$\sqrt{(\bar{r}_0)^2} = \sigma \sqrt{(\bar{S}_0)^2}$$

(C) In actual polymers, different types of interaction forces exist. Cohesive forces ~~be~~ act between polymer chain segments & tighten the coil. ~~In~~ strong interaction and dispersion forces act between segments & solvent molecules; loosening the coil. Thus the actual dimension of the suspended polymer chain depends on the net result of these forces & will be different from $(\bar{r}_0)^2$. In thermodynamically good solvents, strong interaction forces between segment & solvent cause an increase in coil dimension. The increase is described by an expansion factor α

$$\sqrt{r^2} = \alpha \sqrt{(\bar{r}_0)^2}$$

α will be large if polymer molecule is in a good solvent. In a poor solvent α is low since interaction forces are absent & dispersion forces are present. In a non-solvent, dispersion forces are weak. Hence cohesive forces cause tightening of the coil &

the polymer ~~is~~ molecule is squeezed out of solution.

In some solvents bordering between 'poor' & 'non-solvent', the segmental cohesive forces are just ~~&~~ balanced by the solvent dispersion forces and the molecular dimension remains unperturbed by these opposing interactions. Here $\alpha = 1.0$ and $\sqrt{r}^2 = \sqrt{r_0^2}$. For a given polymer & solvent, ~~at~~ the temperature at which α becomes unity is called Flory's theta temperature (θ) and the solvent at that temperature is called 'theta solvent' for that polymer. The same solvent above θ temp. behaves like a 'poor' solvent & as a 'non-solvent' below θ .

Defn of θ Temp. = The temperature at which polymer molecules are just held in solution or are at the threshold of precipitation.

α varies with molecular wt for a given polymer in a given solvent. $\alpha \uparrow$ if $M \uparrow$ or $(\alpha) \propto (M)$.

note 3
end

Flory & Fox deduced an empirical relationship connecting the hydrodynamic volume with the intrinsic viscosity. (This is based on Einstein's theory of viscosity, which states that the specific viscosity of a suspension of spheres in a liquid is proportional to the volume fraction of the spheres.)

The Flory & Fox showed that the ~~hydrodynamic~~ hydrodynamic volume is proportional to the cube of r.m.s. end to end distance (perturbed).

$$[\eta] = \frac{\phi [\bar{r}^2]^{3/2}}{M} \quad (39)$$

Table where ϕ is a universal constant of polymer type, solvent and temperature. When $[\eta]$ is expressed in dl/g, $\phi = 2.84 \times 10^{21}$.

Since $\bar{r}^2 = \alpha^2 \bar{r}_0^2$

$$[\eta] = \phi \left(\frac{\bar{r}_0^2}{M} \right)^{3/2} M^{1/2} \alpha^3 \quad (\bar{r}_0 = \text{unperturbed rms}) \quad (40)$$

$K_\theta = \phi \left(\frac{\bar{r}_0^2}{M} \right)^{3/2}$ is a constant for a polymer and is independent of solvent & temperature.

Final Flory-Fox eqn for mol. wt determination is

$$[\eta] = K_\theta M^{1/2} \alpha^3 \quad (41)$$

At Flory's theta temperature, when α becomes 1.0, the eqn is reduced to

$$[\eta]_\theta = K_\theta M^{1/2} \quad (42)$$

where $[\eta]_\theta$ is the intrinsic viscosity at the theta temperature in a theta solvent.

\therefore in a θ solvent knowledge of α is not required. K_θ alone is sufficient to measure ~~viscosity~~ M with a knowledge of η .

θ solvents are known for limited polymers and

even a very slight variation in the temp. condition makes the system shift from θ conditions.

Attempts were made to compute viscosity functions that would closely resemble $[\eta]_0$ from measurements made in ~~too~~ common solvents at ambient temperature.

Gundiah and Kapur used a plot of η_{sp}/c vs c

~~where~~ $[\eta_{sp}] = \text{specific viscosity ; } c = \text{concentration}$

Note
① (η_{sp}) or specific viscosity = The relative viscosity of a polymer solution of known concentration minus 1, usually determined at low concentration of the polymer e.g. 0.5 gm/100 ml of solution or less.

~~② $[\eta]$ Inherent viscosity = The quotient of the natural logarithm of relative viscosity and the concentration.
Inherent viscosity is $\eta_{inh} = \frac{\eta_{rel}}{c}$ rel = relative
c = conc.~~

③ $[\eta]$ Intrinsic viscosity = Ratio of a solution's specific viscosity to the concentration of the solute, extrapolated to zero concentration. Intrinsic viscosity reflects the capability of a polymer in solution to enhance the viscosity of the solution.
Viscosity behaviour is used to characterize polymers in solution. $[\eta]$ is the limiting value of the specific viscosity/concentration ratio at zero concentration. It is determined by measuring the relative viscosity

at several different concentrations ~~of~~ and then extrapolating the sp. viscosity to zero concentrations. The variation of viscosity with concentration depends on the type of molecule as well as solvent.

Intrinsic viscosity of linear macromolecules is related to the Mol. wt ~~of~~ or degree of polymerization.

Viscosity measurements can be used to determine Mol. wt of linear macromolecules when viscosity vs Mol. wt relationship has been established.

Intrinsic viscosity is calculated by determining reduced viscosity η_{sp}/c & extrapolating to infinite dilution.

$$[\eta] = \lim_{c \rightarrow 0} \eta_{red} \quad \text{Huggins eqn}$$

$$= \lim_{c \rightarrow 0} \eta_{inh} \quad \text{Craemer's eqn}$$

④ $(\eta_{red}) = \text{reduced viscosity} = \text{Sp. viscosity/conc.}$
expressed in g/ml Also known as viscosity no.

$$\eta_{red} = \frac{\eta_{rel} - 1}{c} \quad \boxed{\eta_{rel} = \eta_{relative}}$$

⑤ $\eta_{rel} = \text{ratio of viscosities of polymer solution of stated concentration \& pure solvent at same temp. Also called solution solvent viscosity ratio}$

$$\eta_{rel} = \frac{\rho_1 (C_1 t_1 - E_1/t_1^2)}{\rho_0 (C_0 t_0 - E_0/t_0^2)} \quad \rho = \text{density} \quad C = \text{tube calibration constant (CSt/s)}$$

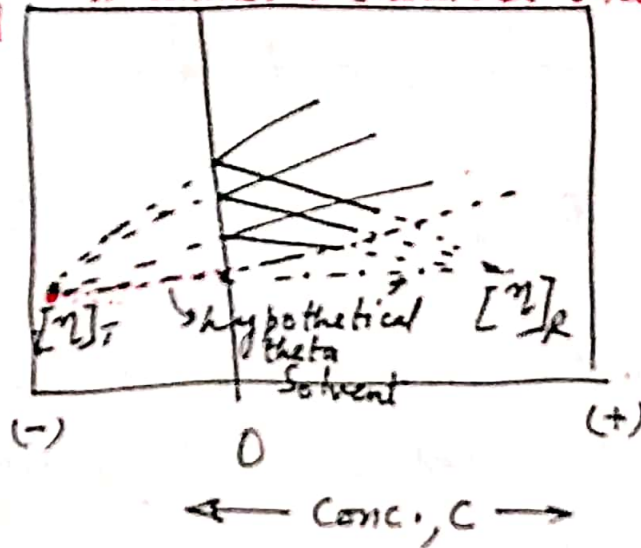
$E = \text{K.E. correction const. (CSt.s}^2)$

note end

Cleverdon & Smith $\rightarrow \eta_{sp}/c$ vs c plots converge to true intrinsic viscosity $[\eta]_T$ when extrapolated to $-ve$ concentrations. & claimed that η unlike η should be independent of the solvent

But $[\eta]_T$ was found to be lower than $[\eta]_0$

But k' alone cannot define slope hence plot can't give $[\eta]_0$ at zero conc. (Grundiah & Kapur)



\uparrow
 $\ln \eta_r/c$

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (36)$$

$$\ln \frac{\eta_r}{c} = [\eta] + k''[\eta]^2 c \quad (37)$$

k', k'' = constant for given polymer/solvent/temp. 5/m

Extrapolation of η_{sp}/c and $\ln \eta_r/c$ plots for

Computing η_T and η_{PR} respectively $[\eta]_T < [\eta]_R$

Grundiah & Kapur put forward an alternative method of extrapolating the $\ln \eta_r/c$ vs c plots to a +ve concentration and showed that such curves meet at a common point of intersection. They termed the intrinsic viscosity ^{at that point} as $[\eta]_R$. According to them, the plots of a hypothetical θ solvent should meet at the same point and since the slope of that point would be zero, $[\eta]_R$ should be identical with $[\eta]_0$.

$$[\eta]_R = [\eta]_0 = K_0 M^{1/2} \quad (43)$$

Further, $[\eta]_R$ are believed to be close to $[\eta]_0$ and can be used to compute M using (43)

12.6.2

p. 282 Unperturbed dimension & intrinsic viscosity

$$\text{Meas } [\eta]_{\theta} = \phi \left(\frac{\bar{r}_0^2}{M} \right)^{3/2} M^{1/2}$$

(44)

* Measurement of viscosities at θ conditions demands exacting experimental conditions.

Moreover, θ temperatures may not lie in a convenient experimentally realisable range.

\therefore Attempts were made to compute the unperturbed dimensions from viscosity measurements using any solvent under normal conditions

Stockmayer and Fixman eqn: - (S&F eqn)

$$[\eta] = k_{\theta} M^{1/2} + 0.51 \phi B M$$

(45)

$$B = \bar{v}_p^2 (1 - 2\chi) / \bar{v}_s N_A$$

(46)

χ = Flory huggins interaction parameter

N_A is Avogadro's number

$$\text{Graphical method: } \frac{[\eta]}{M^{1/2}} = k_{\theta} + 0.51 \phi B M^{1/2}$$

(S&F eqn)

(47)

If the molecular wts of a series of fractions of a polymer & their corresponding intrinsic viscosities in any single solvent at any temp. are known, a simple plot of $[\eta]/M^{1/2}$ vs $M^{1/2}$

will give K_θ as the ordinate intercept.

The unperturbed r.m.s. end to end distance can then be calculated from

$$K_\theta = \phi \left(\frac{\bar{r}_0^2}{M} \right)^{3/2}$$

(48)

χ for the solvent used can also be calculated by knowing the slope of the plot and using $B = \frac{\bar{r}_0^2 (1 - 2\chi)}{V_s N_A}$

12.7

Viscosity of concentrated polymer solution

- Required to understand industrial problems associated with adhesives, coatings, cast films and spun fibres.

In a concentrated solution (> 5.0% polymer) polymer molecules do not exist as isolated chain coils, but are interpenetrating and entangled with each other. Shear effects are therefore, pronounced in such cases. Any viscosity measurement will have to be made at different shear rates & extrapolated to zero shear so as to get the true picture of the solution behaviour. #

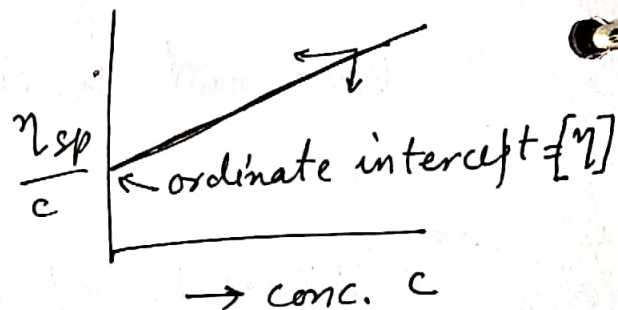
The concentration dependence of viscosity of concentrated solutions can be expressed by

$$\frac{\eta_{sp}}{c(\eta)} = \exp \left\{ \frac{k'[\eta]c}{1-bc} \right\} \quad (49)$$

b is a constant

k' & η can be found out ~~using~~ ^{Huggins} eqn:-

(36) $\rightarrow \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$
 $[\eta]^2 k'$ is the slope



Similarly, viscosity as a fn of Mol. wt and c can be expressed ~~as~~ by the eqn =

$$\eta = K^* [c^{\alpha/\beta} M]^{3.4} \quad (50)$$

K^* is a characteristic constant for a polymer-solvent system and is temperature dependent. Its value is roughly of the order of 2.0×10^{-15} when c is expressed ~~as~~ in g/ml and η in poise. The value of α/β ranges from 1.38 to 1.85 with an average of 1.5.

Viscometry

- * useful technique for determining the polymer mol. wt. \bar{M}_v .
- * Molecular weight obtained = \bar{M}_v .
- * Viscosity of a polymer solution is considerably high as compared to that of the pure solvent.

The increase in viscosity imparted by the macromolecules in solution is a direct function of the hydrodynamic volume & hence, the molecular weight of the macromolecules.

Mark Howink eqn relates η with M

$$[\eta] = K \bar{M}^a$$

where $[\eta]$ is the intrinsic viscosity.

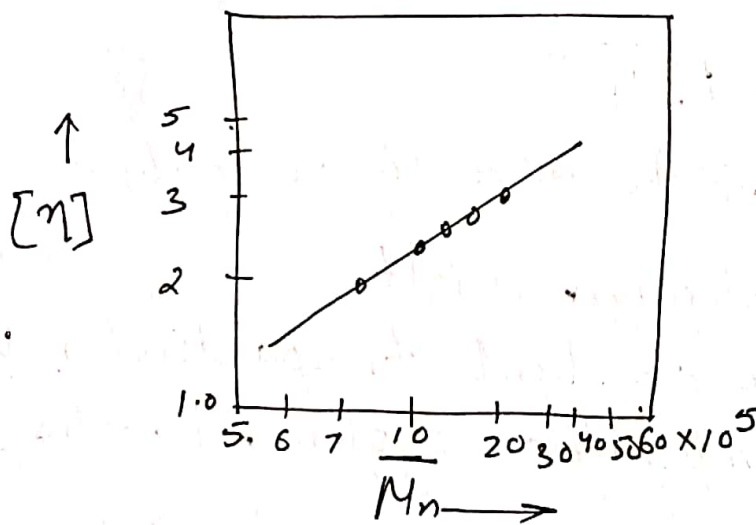
\bar{M} the molecular weight

a & K are constants for a particular polymer & solvent / temperature system. [Tables]

For an unknown polymer system K & a values have to be generated. 1st the sample is fractionated into several fractions, ^{For} and each fraction the molecular wt. is determined by osmometry or by the light scattering technique and η & the corresponding $[\eta]$ are also measured. Table - PTO

Table 13.6 Molecular wt & viscosity data for a poly methyl acetate sample in benzene solution at 30°C.

Fraction no.	Molecular wt $\bar{M}_n \times 10^{-5}$	$[\eta]$ dl/g
1	8.2	1.65
2	11.4	2.19
3	13.9	2.49
4	15.1	2.65
5	19.7	3.20



Plot of $[\eta]$
vs \bar{M}_n
for polymethyl
acetate in
benzene
solution
at 30°C

A log-log plot of $[\eta]$ against \bar{M} gives a straight line.

Slope = a ordinate intercept = K

~~A log~~ $a = 0.725$ $K = 8.63 \times 10^{-5} \text{ dl/g}$

Measurement of $[\eta]$

Assume that a liquid is flowing through a capillary tube. The time required for the liquid of volume V to pass through the capillary of radius r and length l is related to its absolute viscosity η by the famous ~~po~~ Poiseuille eqn as follows: -

$$\eta = \frac{3.14 P r^4 t}{8 V l}$$

$$t = \frac{8 V l \eta}{3.14 P r^4}$$

P is the pressure head under which the liquid flow takes place. If η and η_0 are the absolute viscosities of ~~the~~ a solution and the pure solvent, respectively, & t and t_0 are their corresponding flow times, we can derive the following relationships: -

$$t = \left[\frac{8 V l}{3.14 P r^4} \right] \eta$$

$$t_0 = \left[\frac{8 V l}{3.14 P r_0^4} \right] \eta_0$$

For the same capillary tube the quantities within parenthesis have the same value

Hence we have $\frac{t}{t_0} = \frac{\eta}{\eta_0}$

The term η/η_0 is known as 'relative viscosity'.
This & other terms related to viscosity measurements are as follows: -

Relative viscosity $\frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_r$

Specific viscosity $= (\eta - \eta_0)/\eta_0 = (t - t_0)/t_0 = \eta_r - 1 = \eta_{sp}$

Reduced viscosity $= \eta_{sp}/C = \eta_{red}$, dl/g

Inherent viscosity $= \ln \eta_r / C = \eta_{inh}$, dl/g

Intrinsic viscosity $= (\eta_{sp}/C)_{C \rightarrow 0} = (\ln \eta_r / C)_{C \rightarrow 0} = [\eta]$, dl/g

Intrinsic viscosity is also known as the Staudinger index or limiting viscosity number. As specific viscosity is, by definition, a dimensionless quantity, the intrinsic viscosity has the reciprocal of concentration as its dimension. ~~It may~~ For calculating intrinsic viscosity of a polymer sample in solution, we need not to know the absolute viscosities of the solvent and the solutions but only the flow times

of a constant volume of solvent & the solutions through a particular ~~set~~ ~~to~~ capillary tube. This principle is used in viscometry.

Actual experiment =

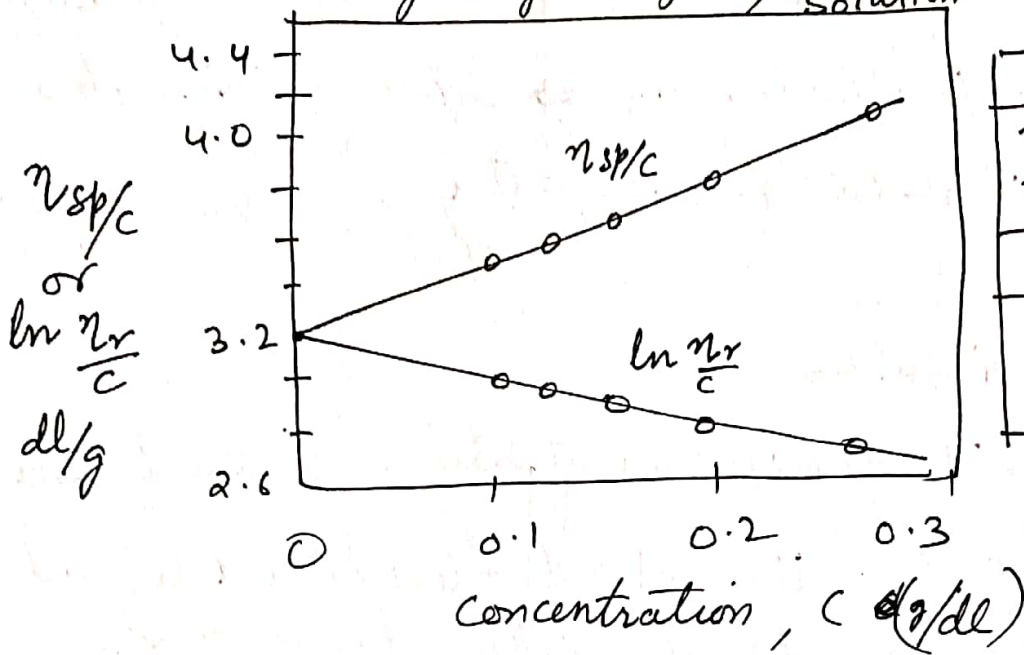
Solutions of known concentrations of the polymer sample are made. The solvent flow time (t_0) and solution flow times (t) for different concentrations are measured using the same viscometer. For each concentration, the corresponding reduced viscosity and the inherent viscosity are calculated.

Subsequently, plots of η_{reduced} & η_{inherent} against concentration are ~~drawn~~ drawn and extrapolated to zero concentration. The common ordinate intercept of these graphs gives the $\eta_{\text{intrinsic}}$ or $[\eta]$

Viscosity data for polymethyl acrylate sample in benzene solution at 30°C ; Flow time for solvent, $t_0 = 216.0$ sec.

Concentration C g/dl	Flow time t sec	$t/t_0 = \eta_r$	$\eta_r^{-1} = \eta_{sp}$	η_{sp}/C dl/g	$\ln \eta_r$	$\ln \eta_r / C$ dl/g
0.27	459.8	2.13	1.13	4.16	0.76	2.78
0.19	378.2	1.75	0.75	3.87	0.56	2.89
0.15	337.9	1.56	0.56	3.74	0.45	2.97
0.12	312.8	1.45	0.45	3.63	0.37	2.99
0.1	296.4	1.37	0.37	3.56	0.31	3.03

Polymethyl acrylate; Benzene; 30°C
solution



Huggins eqn 36

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$

Kraemer eqn 37

$$\ln \frac{\eta_r}{c} = [\eta] - k''[\eta]^2 c$$

Plots of η_{sp}/c vs C & $\ln \frac{\eta_r}{c}$ vs C

The solution viscosities are determined by viscometers (Ostwald & Ubbelohde). These are simple glass capillary devices. All measurements are made using a constant volume of solution in an Ostwald viscometer otherwise the effective pressure head will vary and $\frac{t}{t_0} \neq \frac{\eta}{\eta_0}$. In Ubbelohde; the design is such that the measurement is unaffected by the volume of the solution taken.

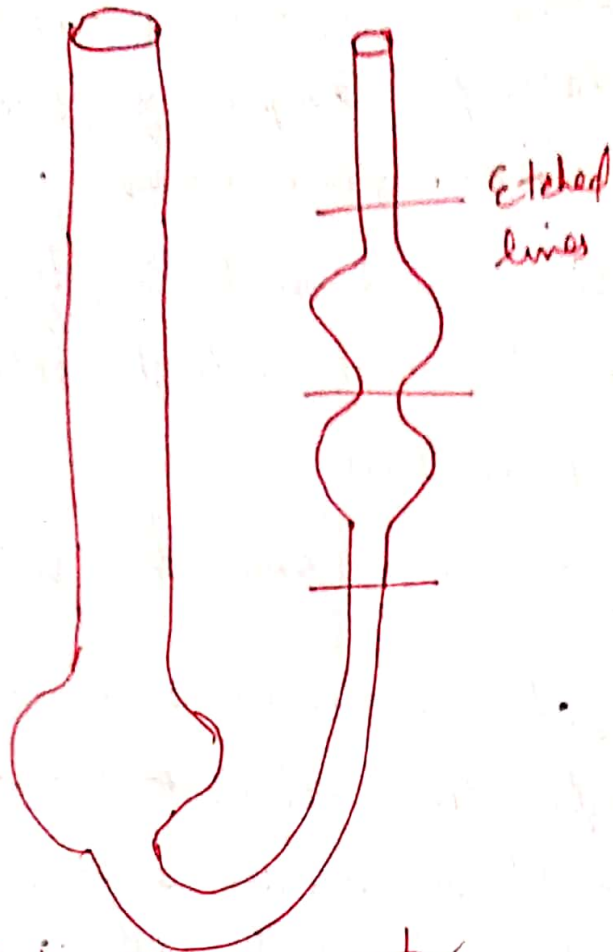
Advantage of Ubbelohde suspended level viscometer, USLV, — Only a single solution of a known concentration is required to be made to start with. A known volume of this solution is taken in the viscometer and the flow time measured. Subsequent concentrations can be achieved by adding known volumes of

pure solvent and mixing inside the viscometer itself. This yields data for computing flow times at different concentrations. In contrast.

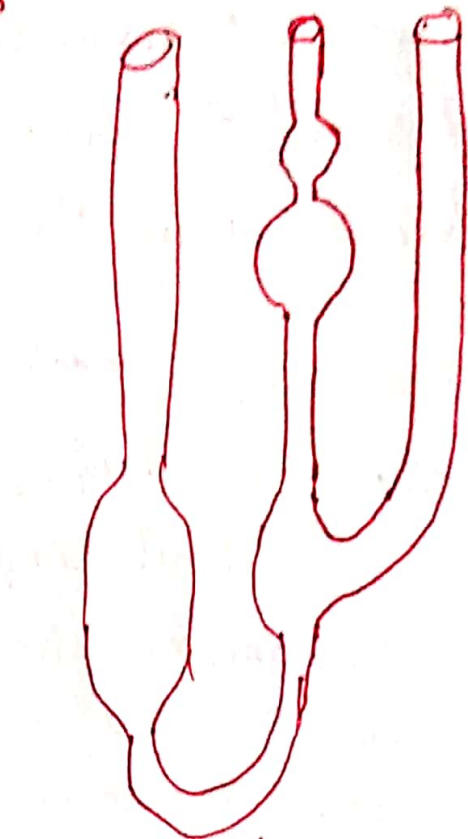
Ostwald → Each time we have to empty, clean and refill the viscometer with a fresh solution before measuring the flow time.

Precautions (for ~~getting~~ ^{obtaining} reproducible results)

- ① Since $\eta \propto \text{Temp.}$, all measurements should be done at a constant temperature within $\pm 0.01^\circ\text{C}$.
- ② The viscometer should be mounted so as to hold the capillary perfectly vertical all the time, otherwise, even with the same volume of the solution the pressure head will vary.
- ③ The flow time for a particular volume of the solution or solvent must be sufficiently long so that the difference in flow time between two successive concentrations is at least of the order of 3 to 5 seconds. (To avoid erroneous measurements)
- ④ All solutions should be free from suspended impurities (obstruction to free flow within capillary will lead to erroneous flow times).



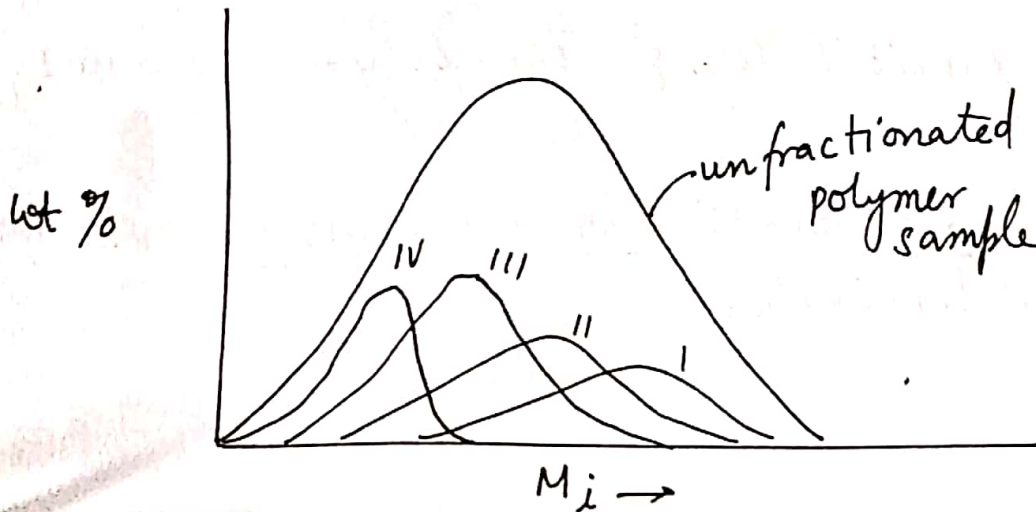
Ostwald viscometer



Ubbelohde
suspended
level viscometer

Measurement
of viscosities of
dilute polymer solutions

Note 1 Polymer fractionation (p 292)



Pattern of molecular wt distribution curve for an unfractionated polymer sample & those for a set of fractions obtainable from it. (I-IV)

Technique → ~~when~~ Principle → When a small quantity of a non-solvent (miscible with the solvent) is added to a polymer solution in a poor solvent, the non-solvent decreases the solvent power further to such an extent that the molecular species of the highest molecular weight can no longer be held in solution and hence, are thrown out of the solution as swollen gel. If the ~~the~~ swollen gel is removed and a further quantity of the non-solvent is added to the remaining solution, the solvent power is further decreased and the molecular species of the next higher molecular weight are thrown out.

In this way, each time some ~~great~~ quantity of the non-solvent is added to a polymer solution, a partial precipitation of the polymer occurs.

Note 2

Table 12.1 (p 279)

Viscosity - molecular weight constants for polymer/solvent systems at 30°C

Polymer	Solvent	$K \times 10^3$ (ml/g)	a
Cellulose trinitrate	ethyl acetate	2.5	1.01
Polybutadiene cis:high trans mix	Toluene	39.0	0.713
Polyethylent terephthalate	Trifluoro acetic acid	43.3	0.68
	Phenol/tetrachloro ethane (3/5 vol)	22.9	0.73

Table 12.2

Viscosity - Mol. wt constants for polyisobutylene in toluene at different temperatures.

Polymer	Solvent	Temp(°C)	$K \times 10^3$ ml/g	a
Polyisobuty- lene	Toluene	0	40	0.6
"	"	15	24	0.65
"	"	30	20	0.67
"	"	50	20	0.68
"	"	60	13.5	0.71