Solution Properties of Polymers

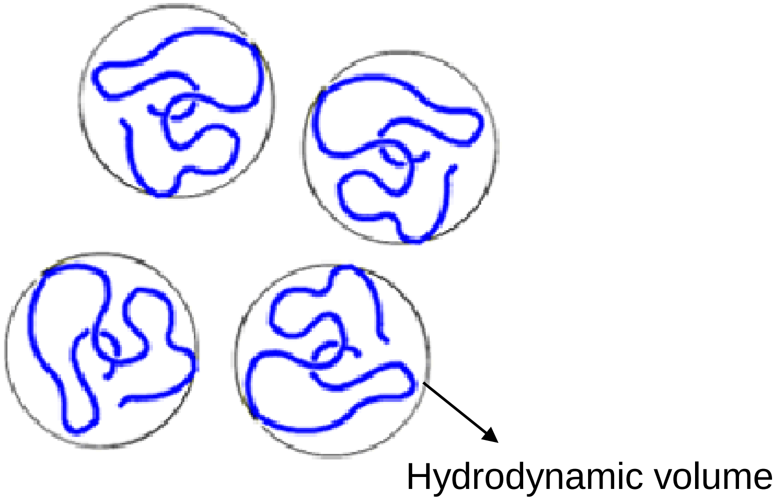
Polymer solubility

Schematic representation of the dissolution process for polymer molecules

a) Polymer molecules in solid state just after being added to a solvent

b) First step: a swollen gel in solvent

c) Second step: solvated polymer molecules dispersed into solution



Solubility depends on;

- ➢Crystalinity
- ➢Molecular weight
- ➢Branching
- ➢Polarity
- ➢Crosslinking degree

Solubility Parameter (Cohesive Energy Density)

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

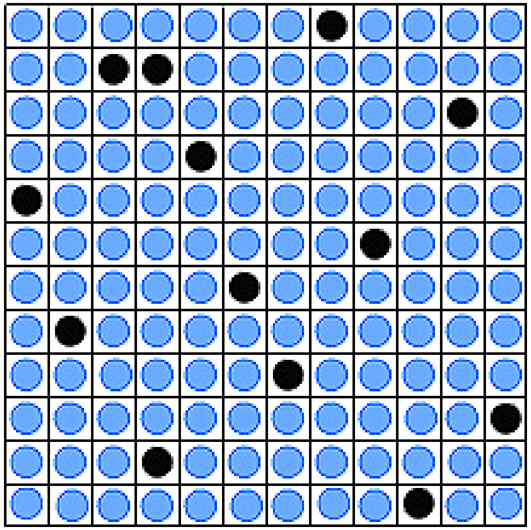
Gibbs free energy

Entropy change during mixing

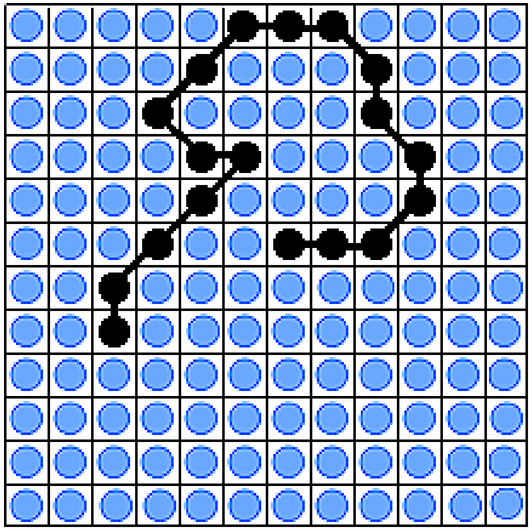
Enthalpy change during mixing

- Solubility will occur if the free energy of mixing ΔGm is negative.
- The entropy of mixing is believed to be always negative.
- Therefore, the sign and magnitude of ΔHm determine the sign of ΔGm.

Two-dimensional lattice model of solubility for a low molecular weight solute



Two-dimensional lattice model of solubility for a polymer solute



The configurational entropy of mixing, given by the Boltzmann equation, is;

$$S = k \ln \Omega$$

where Ω the number of possible arrangements within the lattice, and k the Boltzmann constant.

Hildebrand and Scott showed that;

$$\Delta H_m = \enclose{circle}{V}\,\enclose{circle}{\phi_1\phi_2}\left[\left(\frac{\enclose{circle}{\Delta E_1^v}}{\enclose{circle}{V_1}}\right)^{1/2} - \left(\frac{\enclose{circle}{\Delta E_2^v}}{\enclose{circle}{V_2}}\right)^{1/2}\right]^2 \tag{1}$$

V, V_1, V_2 are the volumes of the solution, and the components and the subscripts 1 and 2 denote the solvent and the polymer, respectively

ΔE^v is the molar energy of vaporization

ϕ_1 and ϕ_2 are volume fractions

Heat of mixing per unit volume;

$$\frac{\Delta H_m}{V} = \phi_1\phi_2\left[\left(\frac{\Delta E_1^v}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2}\right)^{1/2}\right]^2 \tag{2}$$

The quantity ΔE/V is referred to as the cohesive energy density (CED), its square root is the solubility parameter (δ).

$$\boxed{\mathrm{CED} = \frac{\Delta E}{V} = \delta^2} \qquad (3)$$

Equation 2 can be rewritten as;

$$\boxed{\frac{\Delta H_m}{V} = \phi_1 \phi_2 [\delta_1 - \delta_2]^2} \qquad (4)$$

To a first approximation and in the absence of strong intermolecular forces like hydrogen bonding, a polymer is expected to be soluble in a solvent if $\delta_1 - \delta_2$ is less than 1.7–2.0.

Equation 4 is valid only when ΔH_m is zero or greater. It is invalid for exothermic mixing, that is, when ΔH_m is negative.

solvent	δ_s (MPa$^{1/2}$)	Polymer	δ_p (MPa$^{1/2}$)
Acetone	**20.3**	**Polybutadiene**	**14.6-17.6**
Benzene	**18.8**	**Polychloroprene**	**15.2-19.2**
Carbon Tetrachloride	**17.6**	**Polyethylene**	**15.8-18.0**
Chloroform	**19.0**	**Polyisobutylene**	**14.5-16.5**
Cyclohexane	**16.8**	**Polypropylene**	**18.9-19.2**
Ethanol	**26.0**	**Polyacrylonitrile**	**25.3-31.5**
n-Hexane	**14.9**	**Polymethylmethacrylate**	**18.4-26.3**
Methanol	**29.7**	**Polyvinyl acetate**	**18.0-19.1**
Methylene Chloride	**19.8**	**Polyvinyl alcohol**	**25.8**
n-Pentane	**14.3**	**Polyvinyl chloride**	**19.2-22.1**
Toluene	**18.2**	**Polystyrene**	**17.4-21.1**
Water	**47.9**	**Nylon 6.6**	**27.8**

Solubility parameters for solvents and polymers more commonly used.

The solubility parameter can also be estimated from the **molar attraction constants**, E, using the structural formula of the compound and its density For a polymer;

$$\delta_2 = \frac{\rho \sum E}{M}$$

Molar attraction constant

density of the polymer

molecular weight of the repeating unit

Example : Let's now estimate the solubility parameters of following polymers;

a. Low-density polyethylene (HDPE)

b. High-density polyethylene (LDPE)

c. Polypropylene (PP)

d. Polystyrene (PS)

Molar Attraction Constants, E (cal cm^3)/mol

Group	E	Group	E
–CH$_3$	148	NH$_2$	226.5
–CH$_2$–	131.5	–NH–	180
>CH–	86	–N–	61
>C<	32	C› N	354.5
CH$_2$›	126.5	NCO	358.5
–CH›	121.5	–S–	209.5
>C›	84.5	Cl$_2$	342.5
–CH› aromatic	117	Cl primary	205
–C› aromatic	98	Cl secondary	208
–O– ether, acetal	115	Cl aromatic	161
–O– epoxide	176	F	41
–COO–	326.5	Conjugation	23
>C–O	263	*cis*	–7
–CHO	293	*trans*	–13.5
(CO)$_2$O	567	six-membered ring	–23.5
–OH–	226	ortho	9.5
OH aromatic	171	meta	6.5
–H acidic dimer	–50.5	para	40

From Hoy, K.L., *J. Paint Technol.*, 42, 76, 1970. With permission.

Dilute Polymer Solutions

“Shape" or magnitude of the random coil will depend on;

- the kind of solvent employed
- the temperature
- the molecular weight

Random coil model

<u>The polymer-solvent interactions play an important role in this case, and its magnitude, from a thermodynamic point of view, will be given by the solvent quality.</u>

<u>In a "good" solvent,</u> that is to say that one whose solubility parameter is similar to that of the polymer, the attraction forces between chain segments are smaller than the polymer-solvent interactions; the random coil adopts then, an unfolded conformation.
<u>In a "poor" solvent,</u> the polymer-solvent interactions are not favored, and therefore attraction forces between chains predominate, hence the random coil adopts a tight and contracted conformation.
<u>In extremely "poor" solvents,</u> polymer-solvent interactions are eliminated thoroughly, and the random coil remains so contracted that eventually precipitates.

We say in this case, that the macromolecule is in the presence of a "non-solvent".

Dilute Polymer Solutions

Imagine a polymer dissolved in a "good" solvent. If a non-solvent is added to this solution, the attractive forces between polymer segments will become higher than the polymer-solvent interactions. At some point, before precipitation, an equilibrium will be reached,

$$\Delta G = 0 \;\rightarrow\; \Delta H = T\Delta S$$

θ or flory temperature

where ΔS reaches its minimum value

This point, where polymer-solvent and polymer-polymer interactions are of the same magnitude, is known as ***θ (theta) state.***

- ➢the temperature
- ➢the polymer-solvent system
- ➢ the molecular weight

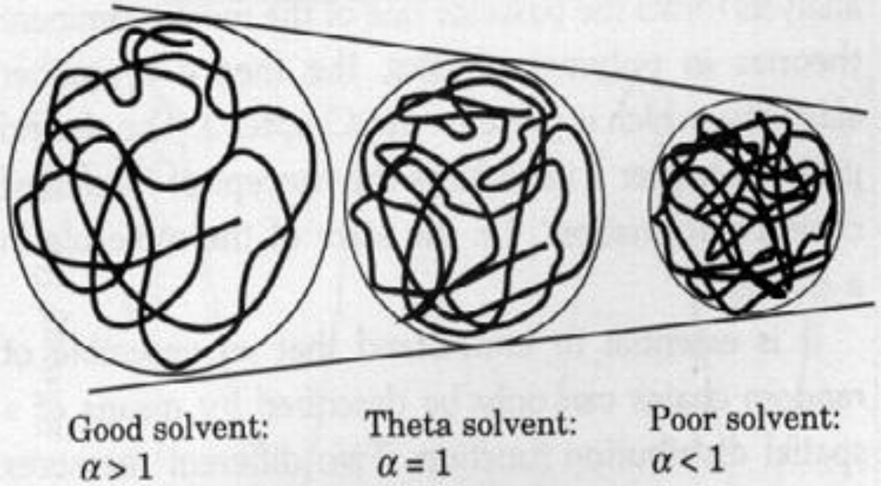
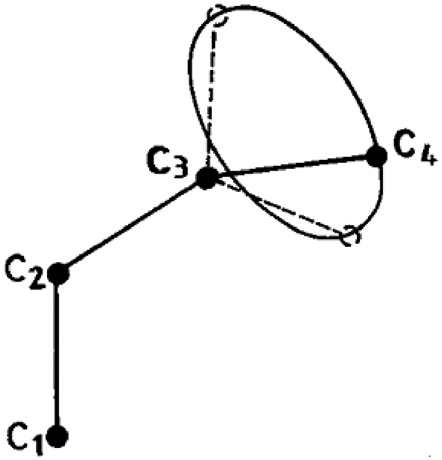


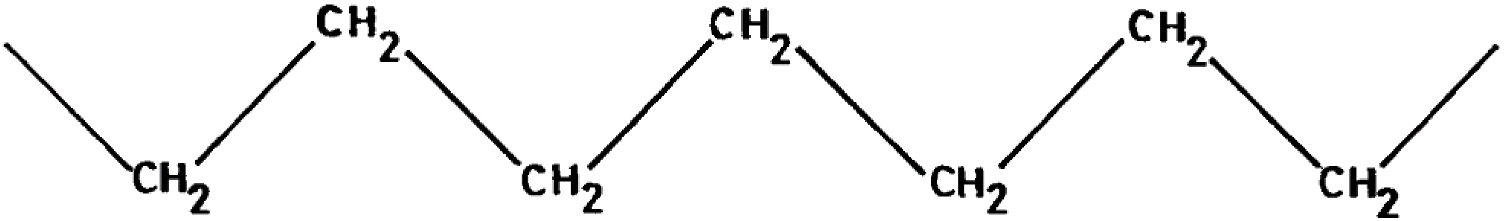
Figure 2.7 Random coils in solvents of different solvent power; α Lineer yumak genleşme faktörü

Polymer	Solvent(s)	θ temperature (°C)
Polyethylene	n-Hexane	133
	n-Hexanol / Xylene (70:30)	170
	n-Octane	210
Polypropylene (atactic)	n-Butanol / Carbon Tetrachloride (33:67)	25
	n-Butanol / n-Hexane (32:68)	25
	Cyclohexanone	92
Polystyrene	Benzene / n-Butanol (58:42)	35
	Cyclohexane	34-35
	Cyclohexanol	79-87
Poly (vinyl acetate)	Ethanol	19
	Ethanol / Methanol (40:60)	36
Poly (vinyl alcohol)	Ethanol / Water (41.5-58.5)	25
	Water	97
Poly (vinyl chloride)	Cyclohexanone	22
	Dimethylformamide	36.5
Polyacrylamide	Methanol / Water (2:3)	20
Polymethylmethacrylate	Acetone	-126
	Cyclohexanol	77.6
	Toluene	-65
	Dioxane / Water (85:15)	25

Conformations of Polymer Chains in Solution



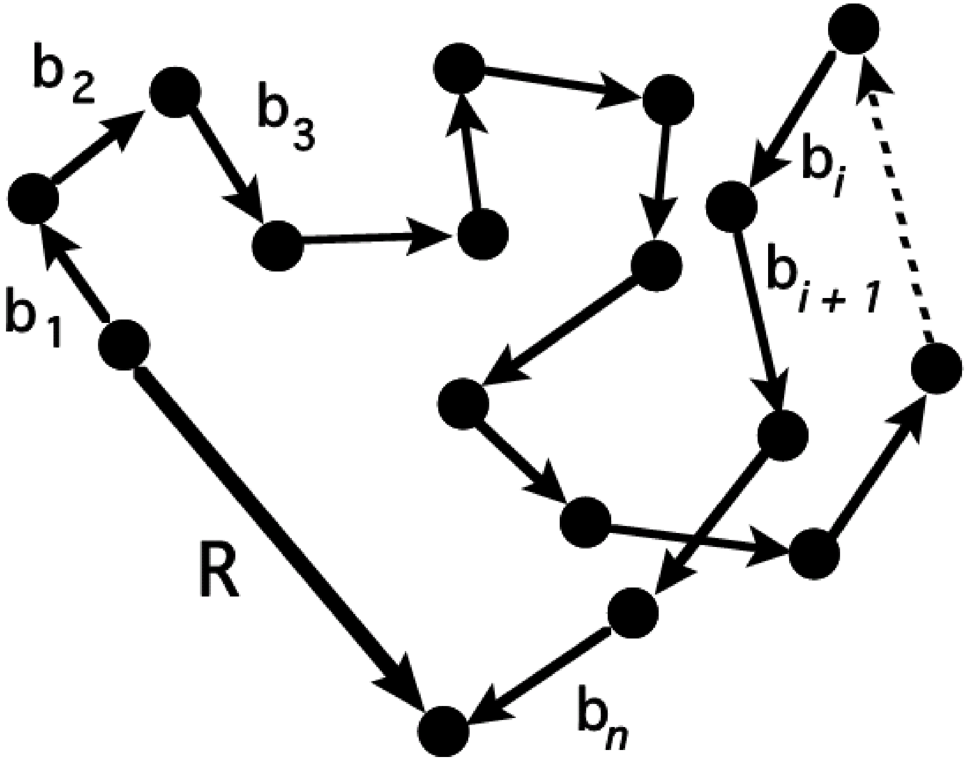
A segment of a polymer chain, showing four successive chain atoms. The first three of these define a plane, and the fourth can lie anywhere on the indicated circle perpendicular to and bisected by the plane.



Fully extended chain with every carbon atom in trans *location and in the same plane.*

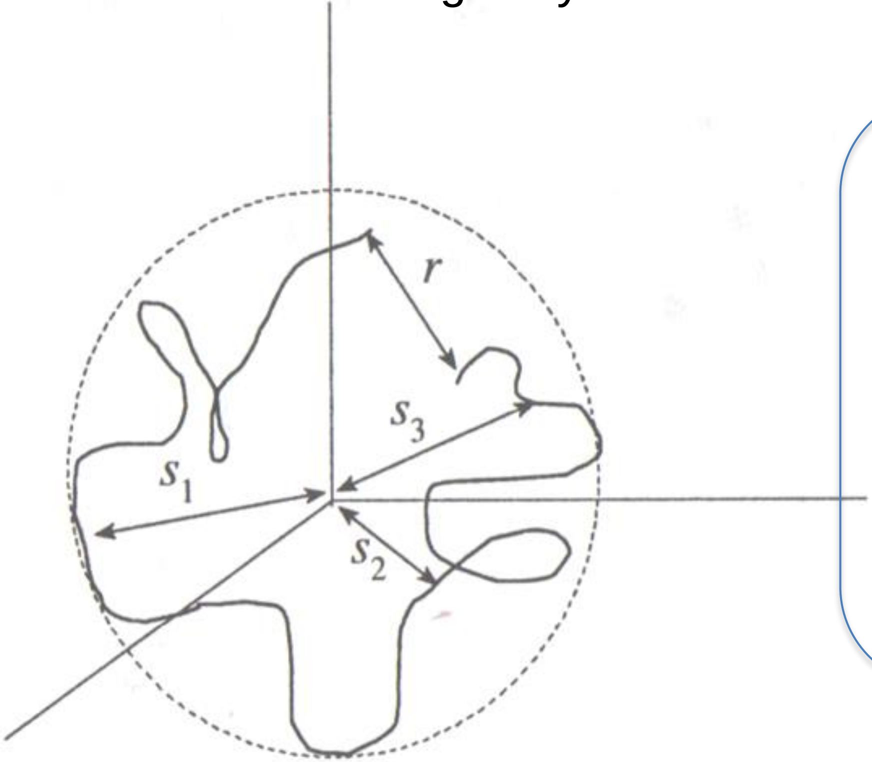
End-to-End Dimensions

End to end distance is the the polymer dimension that is most often used to describe its spatial character is the displacement length, which is the distance from one end of the molecule to the other. **For the fully extended chain,** this quantity is referred to as the contour length.



Radius of Gyration (Rg or s)

The radius of gyration is the root-mean-square distance of the elements of the chain from its center of gravity.



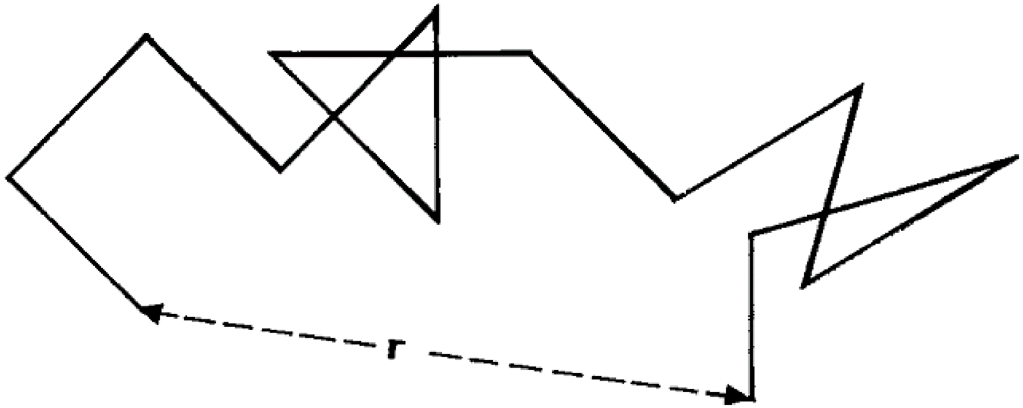
Şekil 3.11 Rastgele bükülmüş bir polimer zinciri için uçtan-uca uzaklık (r) ve jirasyon yarıçapı (s). Zincirin farklı noktaları için örnek jirasyon yarıçapları gösterilmiştir (s_1, s_2, s_3 ... gibi).

For linear polymers;

$$\langle s^2 \rangle^{1/2} = \frac{\langle r^2 \rangle^{1/2}}{6^{1/2}}$$

The freely jointed chain

$$\langle R^2 \rangle = na^2$$

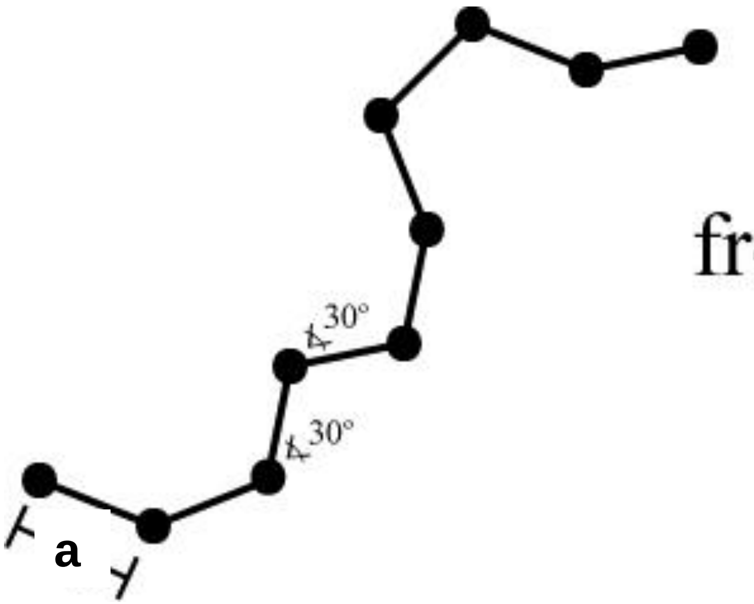


Freely jointed model of a polymer molecule with fixed and equal bond length and unrestricted value of bond angle.

Fixed bond angle (freely rotating)

$$\langle R^2 \rangle = na^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right)$$

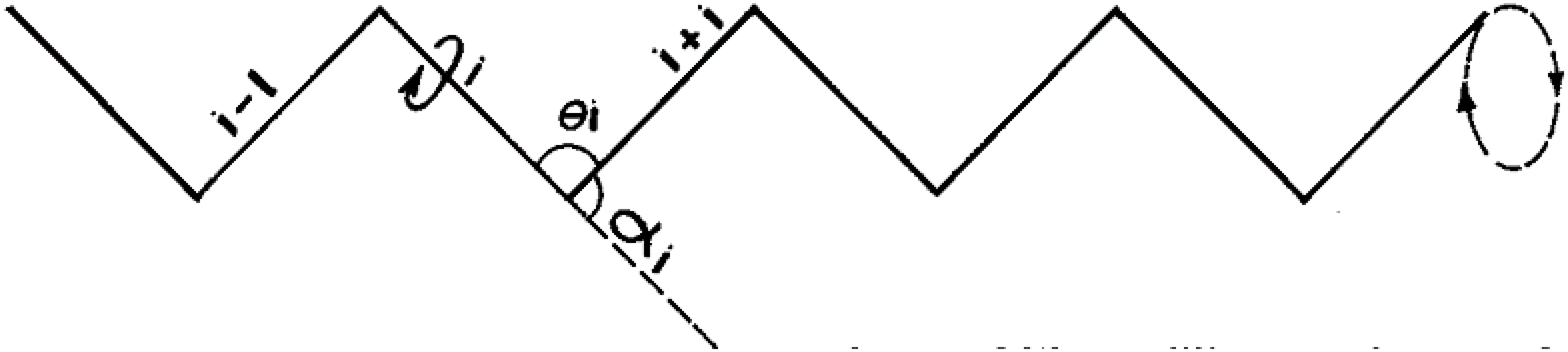
where θ is the bond angle



freely-rotating chain
(drawn in 2D
for θ= 150 °C)

Fixed bond angles (restricted rotation)

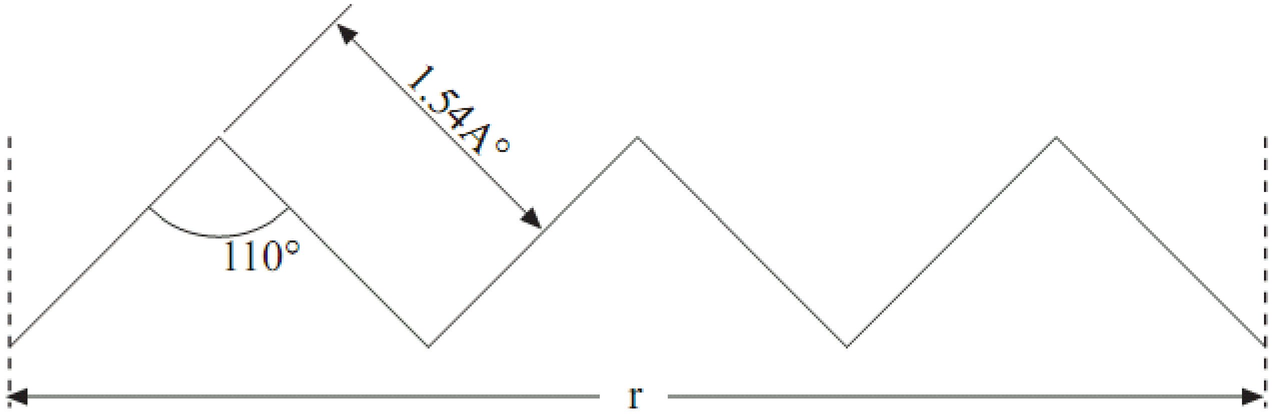
$$\langle R^2 \rangle = na^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \left(\frac{1+\cos\varphi}{1-\cos\varphi} \right)$$



Rotation about bond i.

Example

A polyethylene molecule has a degree of polymerization of 2000.
Calculate
(a) the total length of the chain and
(b) the contour length of the planar zigzag if the bond length and valence angle are 1.54 Å and 110°, respectively.



Solution:

a. The total length of the chain, L, is the sum of the length of each bond, l. It is the total distance traversed going from one end of the chain to the other following the bonds.

b. The contour length is that of the fully extended chain conformation.

Solution Viscosity

Rheology is the science of deformation and flow of matter.

Rheology deals with those properties of materials that determine their response to mechanical force.

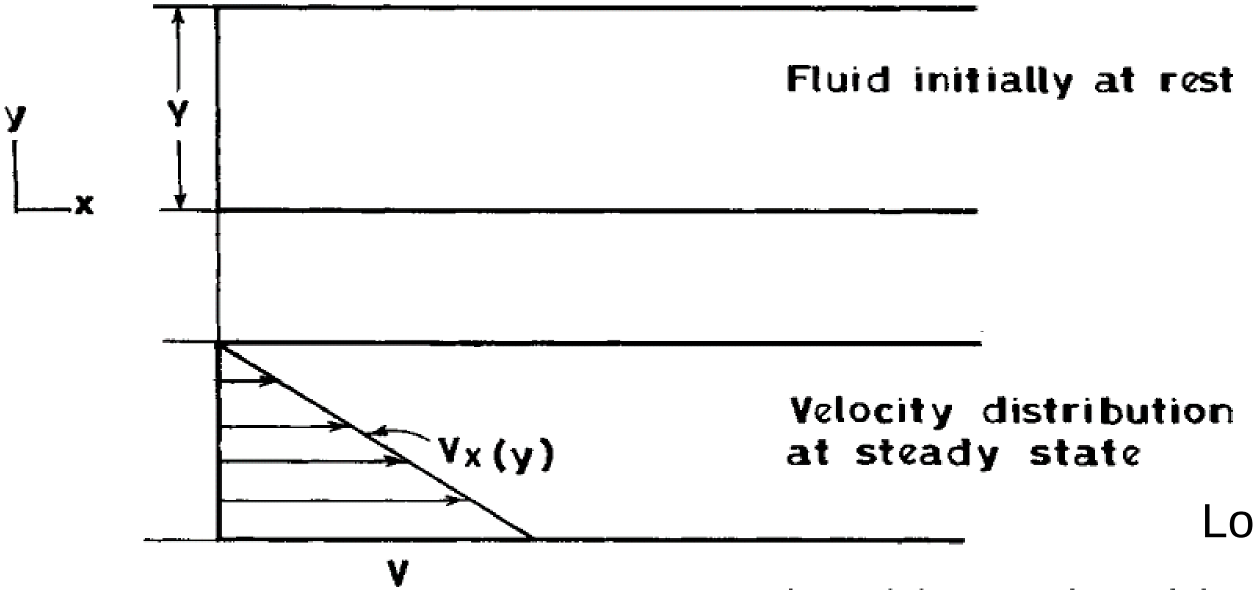
For solids, this involves elasticity and plasticity.
For fluids, on the other hand, rheological studies involve viscosity measurements.

Viscosity is a measure of the internal friction of a fluid.

Measurements of the viscosity of polymer solutions can provide information about;

- **Molecular weight**
- **molecular weight distribution**
- **other material characterization parameters**.

Newton`s law of Viscosity



Laminar velocity profile for fluid between two plates.

$$\frac{F}{A} = \eta \frac{V}{Y} \Longrightarrow \tau_{yx} = -\eta \frac{dV_x}{dy}$$

Viscosity of the fluid

Shear stress

Local velocity gradient

Newton`s law of Viscosity

$$\tau_{yx} = -\eta \frac{dV_x}{dy}$$

Equation states that the shear stress is proportional to the negative of the local velocity gradient.
This is **Newton's law of viscosity**, and fluids that exhibit this behavior are referred to as **Newtonian fluids**.

For a given stress, fluid viscosity determines the magnitude of the local velocity gradient. Fluid viscosity is due to molecular interaction; it is a measure of a fluid's tendency to resist flow, and hence it is usually referred to as the internal friction of a fluid.

Strain rate

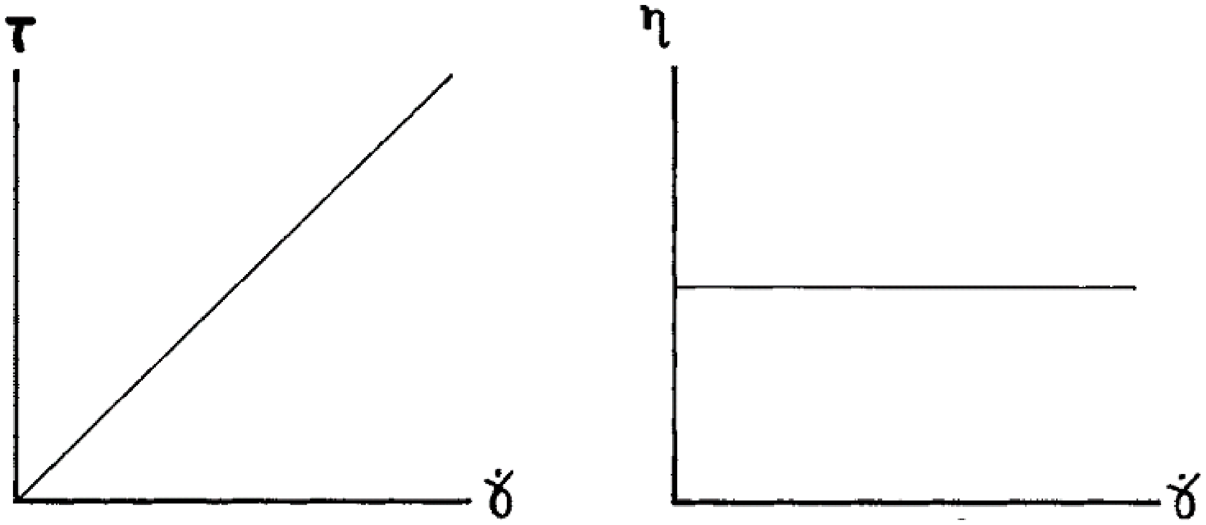
$$\tau_{yx} = -\eta \dot{\gamma}$$

$$\frac{dV}{dy} = \frac{d}{dy}\left(\frac{dx}{dt}\right) = \frac{d}{dt}\left(\frac{dx}{dy}\right) = \frac{d\gamma}{dt} = \dot{\gamma}$$

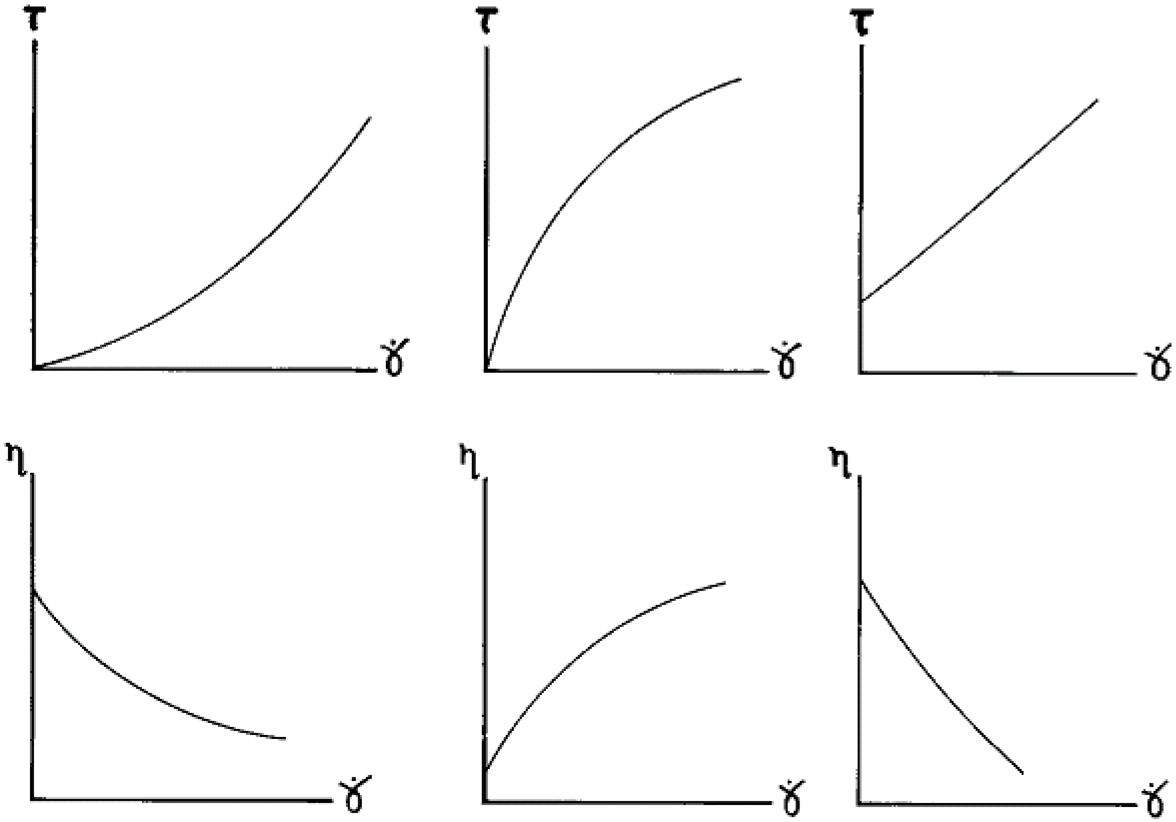
Newton`s law of Viscosity

$$\tau_{\mathrm{yx}} = -\eta \dot{\gamma}$$

- Newton’s law simply states that for laminar flow, the shear stress needed to maintainthe motion of a plane of fluid at a constant velocity is proportional to the strain rate.
- At a given temperature, the viscosity of a Newtonian fluid is independent of the strain rate



Behavior of Newtonian fluids.



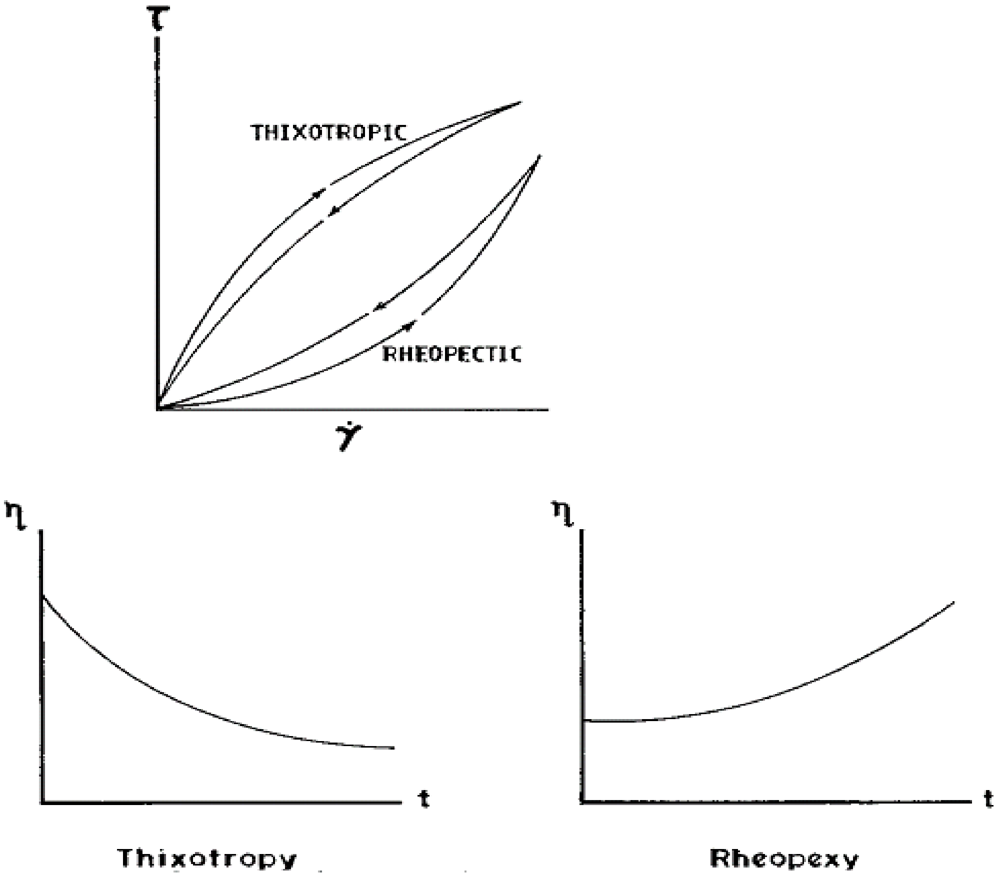
Pseudoplastic
(a)

Dilatant
(b)

Plastic
(c)

Some types of non-Newtonian behavior.

Pseudoplastic fluids display a decrease in viscosity with increasing strain rate, while a **dilatant fluid** is characterized by an increase in viscosity with increasing strain rate. For fluids that exhibit **plastic behavior**, a certain amount of stress is required to induce flow. The minimum stress necessary to induce flow is frequently referred to as the yield value.



Thixotropy

Rheopexy

Change of viscosity with time under constant strain rate.

Some fluids will show a change of viscosity with time at a constant strain rate and in the absence of a chemical reaction. Two categories of this behavior are encountered: **thixotropy and rheopexy**. **A thixotropic fluid** undergoes a decrease in viscosity, whereas a **rheopectic fluid** displays an increase in viscosity with time under constant strain rate

Parameters for Characterizing Polymer Solution Viscosity-1

The flow of fluids through a tube of uniform cross-section under an applied pressure is given by the Hagen–Poiseuille's law;

$$Q = \frac{\pi R^4 \Delta P}{8 \eta L} \longrightarrow \Delta P = \Delta h \rho g$$

$$\Delta P = \Delta h$$

where Q is the volume flow rate (dV/dt), ΔP is the pressure drop across the tube of length L and radius R.

$$\boxed{\eta = \frac{\pi R^4 \Delta h \rho g t}{8 l V}}$$

Factors affecting viscosity

- Polymer and solvent type
- Molecular weight of polymer
- Concentration of polymer
- Temperature

Flow time of solution

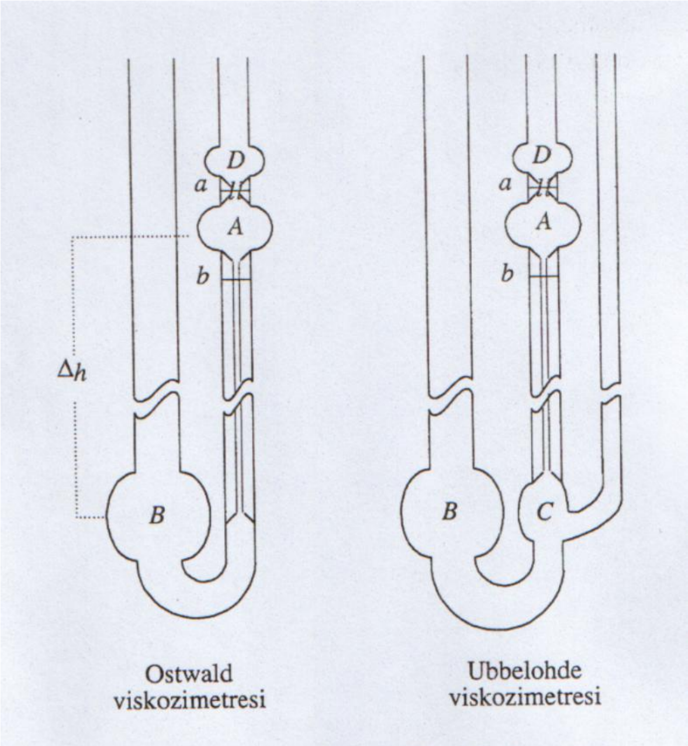
Viscosity of solution

$$\eta = \frac{\pi R^4 \Delta p t}{8lV}$$ (solution)

Flow time of solvent

Viscosity of pure solvent

$$\eta_o = \frac{\pi R^4 \Delta p_o t_o}{8lV}$$ (solvent)



Şekil 3.15 *Ostwald* ve *Ubbelohde* viskozimetreleri.

Viscosity of the solution

$$\eta_r = \frac{\eta}{\eta_o} = \frac{t}{t_o}$$

Relative viscosity

Viscosity of the pure solvent

Parameters for Characterizing Polymer Solution Viscosity-2

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

Specific viscosity

Huggings constant, with a value in the range of 0.35-0.4

$$\eta_{sp} = [\eta]c + \mathrm{k}^{`}[\eta]^2 c^2 + \ldots\ldots.$$

Concentration of polymer

$$reduced\ viscosity = \frac{\eta_{\mathrm{sp}}}{c}$$

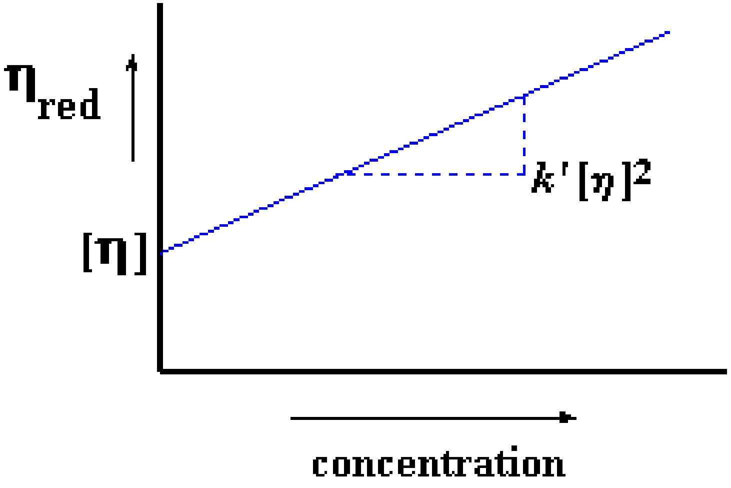
When $\eta_r<2$, it has been found that the linear relation exists between the reduced viscosity and polymer concentration.

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

Intrinsic Viscosity

The intrinsic viscosity [η] is the limiting value of the reduced viscosity at infinite dilution.

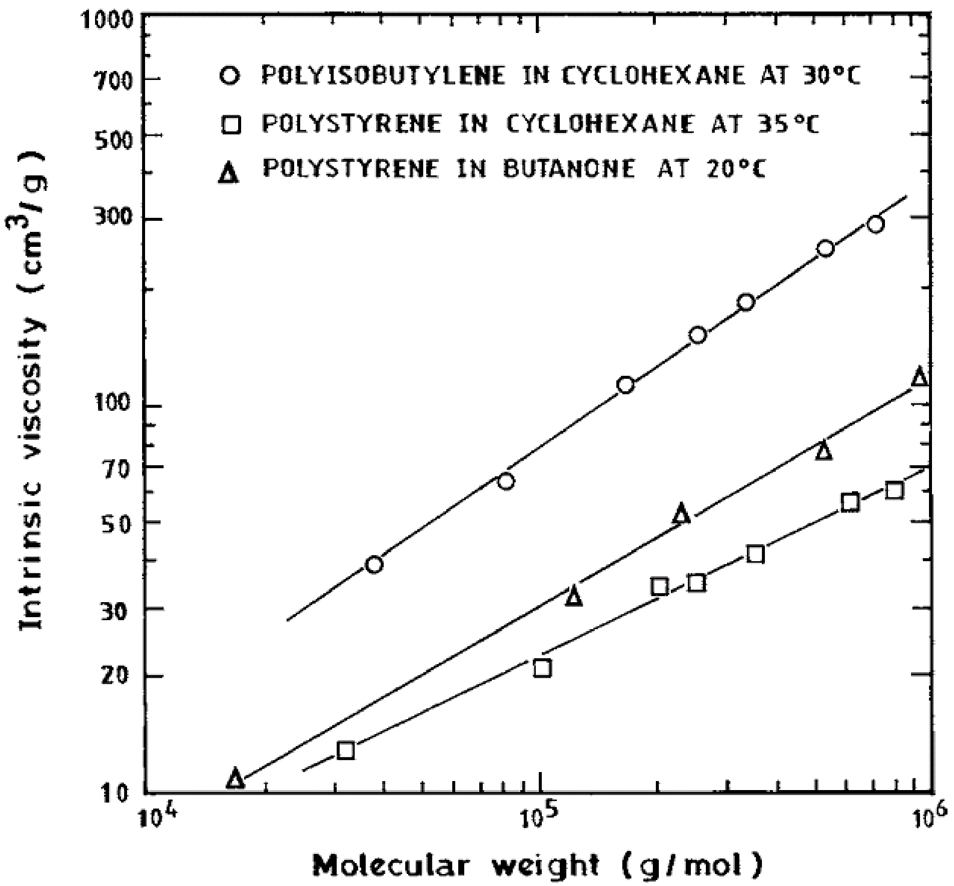
$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c}$$



A plot of reduced viscosity vs. concentration.
We call the *y*-intercept [*η*], or the intrinsic viscosity.
The slope is related to [*η*], it's equal to *k*'[*η*]^2.

Viscosity Term	Expression	Unit
Solution viscosity	η	Poise (g/cms)
Solvent viscosity	η_o	Poise (g/cms)
Relative viscosity	$\eta_r=\eta/\eta_0$	Unitless
Specific viscosity	$\eta_{sp}=(\eta-\eta_0)/\eta_0=\eta_r-1$	Unitless
Reduced viscosity	$\eta_{sp}/c=(\eta_r-1)/c$	cm^3/g
Intrinsic viscosty	$[\eta]=\lim_{c\to 0}\frac{\eta_{sp}}{c}$	cm^3/g

Molecular Weight From Intrinsic Viscosity



Intrinsic viscosity–molecular weight relationship. (From Allocock, H.R. and Lampe, F.W., Contemporary Polymer Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1981. With permission.)

The slopes of these curves for **a given polymer depend on the solvent** and, for a given polymer–solvent pair, **on the temperature**. It has been established that the slopes of such plots for all polymer–solvent systems fall within the range **of 0.5 to 1.0.**

Molecular Weight From Intrinsic Viscosity

Mark-Houwink Equation

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

K and a are constants determined from the intercept and slope of plots

$\overline{M}_v$ is the viscosity average molecular weight.

$$\overline{M}_v = \left[\sum \omega_i M_i^{a}\right]^{1/a} = \left[\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i}\right]^{1/a}$$

Melt Flow Index (MFI)

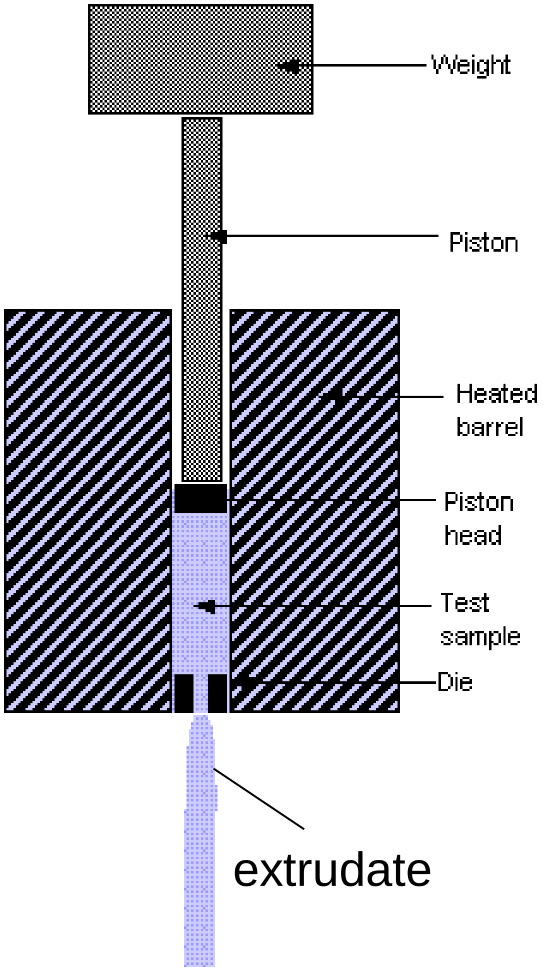
- The **Melt Flow Index** is a measure of the ease of flow of the melt of a thermoplastic polymer or a measure of the ability of the material's melt to flow under pressure.

- It is defined as the weight of polymer in grams flowing in 10 minutes through a capillary of specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures.

- The melt flow rate is an indirect measure of molecular weight, high melt flow rate corresponding to low molecular weight.

- The melt flow rate is inversely proportional to the viscosity of the melt at the conditions of the test

Melt Flow Index (MFI) Apparatus



- ❑Comprises a cylinder containing polymer melt which loaded from above by a piston carrying a weight.

- ❑There is a capillary die at the bottom of the cylinder

- ❑The procedure is to measure the output by cutting off sections of extrudate at known time intervals and weighing them