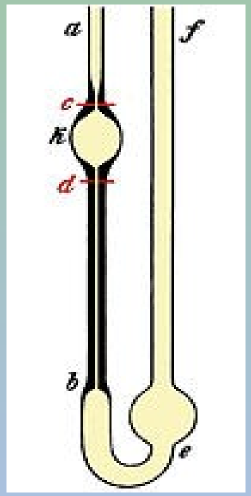
Polymerization kinetics:

- The molecular weight of polymer,
- Measurement of molecular weight and molecular weight distribution
- General rate of reaction and kinetic investigations

Molecular weight and distribution of polymers

Polymers are high molecular mass compounds formed by polymerization of monomers. Therefore Polymers in solution have special characteristics with respect to solubility, viscosity, and gelation. The viscosity of polymer solutions is a valued parameter. Viscometers such as this are employed in such measurements.

The molecular weight of a polymer is of prime importance in the polymer's synthesis and application. Chemists usually use the term molecular weight to describe the size of a molecule. The more accurate term is molar mass, usually in units of g/mol.



The interesting and useful mechanical properties that are uniquely associated with polymeric materials are a consequence of their high molecular weight.

Most important mechanical properties depend on and vary considerably with molecular weight as seen in Fig. 1-3.

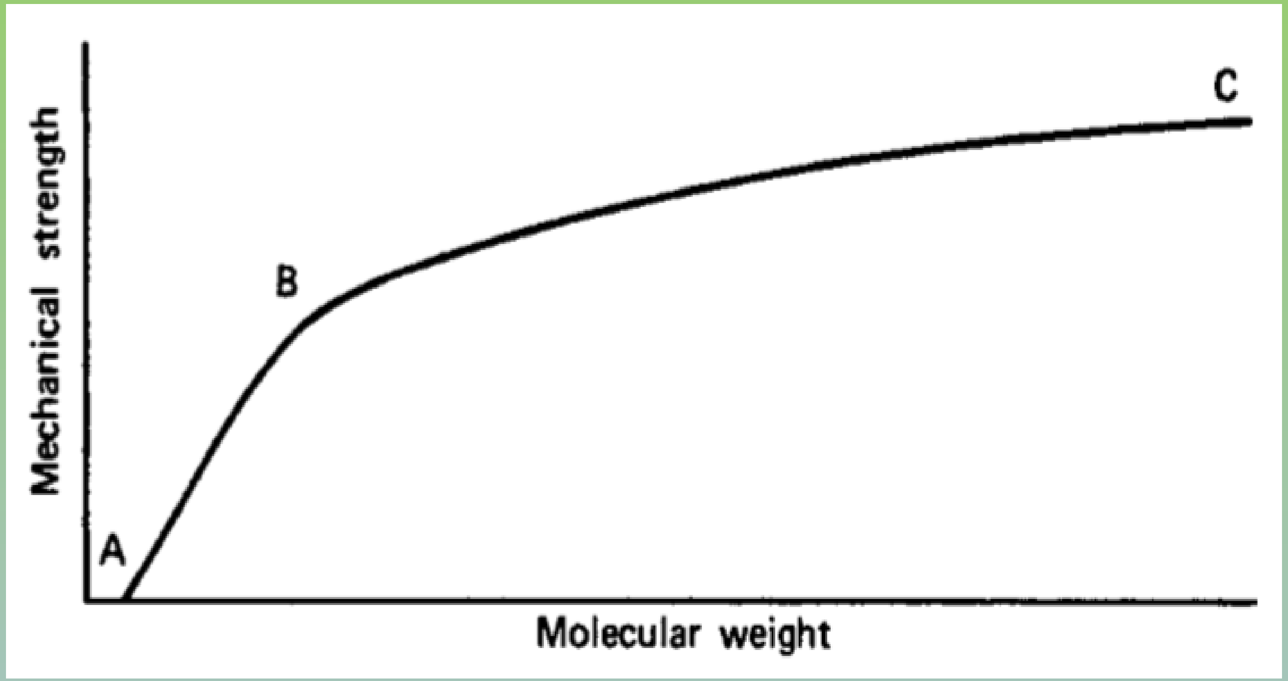


Figure shows dependence of mechanical strength on polymer molecular weight

Polymers differ from the smallsized compounds in that they are polydisperse or heterogeneous in molecular weight. Even if a polymer is synthesized free from contaminants and impurities, it is still not a pure substance in the usually accepted sense. Polymers, in their purest form, are mixtures of molecules of different molecular weight.

When one discusses the molecular weight of a polymer, one is actually involved with its average molecular weight. Both the average molecular weight and the exact distribution of different molecular weights within a polymer are required in order to fully characterize it.

Gel permeation chromatography (GPC) is one of thVarious methods have been used in the past to determine the molecular weight distribution of a polymer sample, including fractional extraction and fractional precipitation.

These methods are laborious and determinations of molecular weight distributions were not routinely performed. However, the development of size exclusion chromatography (SEC), also referred to as gel permeation chromatography (GPC) and the availability of automated commercial instruments have changed the situation. Molecular-weight distributions are now routinely performed in most laboratories using SEC.

The most powerful and versatile analytical techniques available for understanding and predicting polymer performance. It is the most convenient technique for characterizing the complete molecular weight distribution of a polymer.

Why is GPC important? GPC can determine several important parameters. These include number average molecular weight (Mn), weight average molecular weight(Mw) Z weight average molecular weight(Mz), and the most fundamental characteristic of a polymer its molecular weight distribution(PDI)

These values are important, since they affect many of the characteristic physical properties of a polymer. Subtle batch-to-batch differences in these measurable values can cause significant differences in the end-use properties of a polymer. Some of these properties include: Tensile strength Adhesive strength Hardness Elastomer relaxation Stress-crack resistance Adhesive tack Brittleness Elastic modules Cure time Flex life Melt viscosity Impact strength Tear Strength Toughness Softening temperature

Number average molecular weight: Mn The number average molecular weight is the statistical average molecular weight of all the polymer chains in the sample, and is defined by:

$$Mn = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where Mi is the molecular weight of a chain and Ni is the number of chains of that molecular weight. Mn can be predicted by polymerization mechanisms and is measured by methods that determine the number of molecules in a sample of a given weight; for example, colligative methods such as end-group assay. If Mn is quoted for a molecular weight distribution, there are equal numbers of molecules on either side of Mn in the distribution.

Weight average molecular weight: Mw The weight average molecular weight is defined by:

$$Mw = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

$$\overline{M}_w = \sum w_x M_x \qquad (1\text{-}17)$$

where w_x is the weight fraction of molecules whose weight is M_x. $\overline{M}_w$ can also be defined as

$$\overline{M}_w = \frac{\sum c_x M_x}{\sum c_x} = \frac{\sum c_x M_x}{c} = \frac{\sum N_x M_x^2}{\sum N_x M_x} \qquad (1\text{-}18)$$

where c_x is the weight concentration of M_x molecules, c is the total weight concentration of all the polymer molecules, and the following relationships hold:

$$w_x = \frac{c_x}{c} \qquad (1\text{-}19)$$

$$c_x = N_x M_x \qquad (1\text{-}20)$$

$$c = \sum c_x = \sum N_x M_x \qquad (1\text{-}21)$$

Compared to Mn, Mw takes into account the molecular weight of a chain in determining contributions to the molecular weight average. The more massive the chain, the more the chain contributes to Mw. Mw is determined by methods that are sensitive to the molecular size rather than just their number, such as light scattering techniques.

REF: Wendy Gavin Biomolecular Characterization Laboratory Version 1 May 2016, GPC - Gel Permeation Chromatography