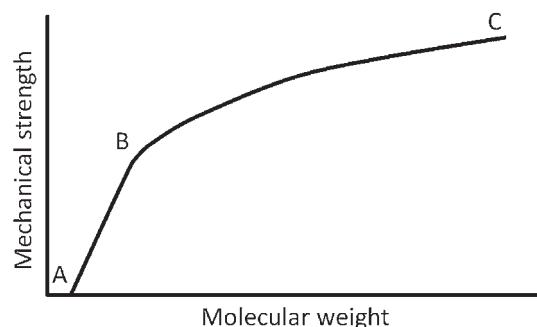# Chapter 2
Polymer Size and Polymer Solutions

The size of single polymer chain is dependent on its molecular weight and morphology. The morphology of a single polymer chain is determined by its chemical structure and its environment. The polymer chain can be fully extended in a very dilute solution when a good solvent is used to dissolve the polymer. However, the single polymer chain is usually in coil form in solution due to the balanced interactions with solvent and polymer itself. We will discuss the size of polymer first, and then go to the coil formation in the polymer solution.

2.1 The Molecular Weight of Polymer

The molecular weight of polymer determines the mechanical properties of polymers. To have strong durable mechanical properties, the polymer has to have molecular weight much larger than 10,000 for structural applications. However, for thin film or other special application, low molecular weight polymer or oligomer sometime is adequate. As shown in Fig. 2.1, above (A), strength increases rapidly with molecular weight until a critical point (B) is reached. Mechanical strength increases more slowly above (B) and eventually reaches a limiting value (C). High molecular weight polymer has high viscosity and poor processability. The control of molecular weight and molecular weight distribution (MWD) is often used to obtain and improve certain desired physical properties in a polymer product.

Polymers, in their purest form, are mixtures of molecules of different molecular weights. The reason for the polydispersity of polymers lies in the statistical variations present in the polymerization processes. The above statement is true for common polymerization reaction such as free radical chain polymerization, step polymerization, etc. However, cationic or anionic chain polymerization as so called living polymerization has small MWD. Low dispersity can also be obtained from emulsion polymerization, and new polymerization techniques such as living free radical polymerization including nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain

Fig. 2.1 Dependence of
mechanical strength on
polymer molecular weight [1]

transfer polymerization (RAFT). The chemistry of different polymerization reactions will be discussed in detail in the subsequent chapters.

Number-average molecular weight ($\bar{M}_n$) is total weight (W) of all the molecules in a polymer sample divided by the total number of molecule present, as shown in Eq. 2.1, where N_x is the number of molecules of size M_x, $\underline{N}_x$ is number (mole) fraction of size M_x

$$\bar{M}_n = W/\Sigma N_x = \Sigma N_x M_x/\Sigma N_x = \Sigma \underline{N}_x M_x \tag{2.1}$$

Analytical methods used to determine $\bar{M}_n$ include (1) $\bar{M}_n < 25{,}000$ by vapor pressure osmometry, (2) $\bar{M}_n$ 50,000–2 million by membrane osmometry, and (3) $\bar{M}_n < 50{,}000$ by end group analysis, such as NMR for –C=C; titration for carboxylic acid ending group of polyester. They measure the colligative properties of polymer solutions. The colligative properties are the same for small and large molecules when comparing solutions at the same mole fraction concentration. Therefore, the $\bar{M}_n$ is biased toward smaller sized molecules. The detailed measurement methods of molecular weight will be discussed in Sect. 2.3. Weight-average molecular weight is defined as Eq. 2.2, where W_x is the weight fraction of M_x molecules, C_x is the weight concentration of M_x molecules, and C is the total weight concentration of all of the polymer molecules, and defined by Eqs. 2.3–2.5.

$$\bar{M}_w = \Sigma W_x M_x = \Sigma C_x M_x/\Sigma C_x \tag{2.2}$$

$$W_x = C_x/C \tag{2.3}$$

$$C_x = N_x M_x \tag{2.4}$$

$$C = \Sigma C_x = \Sigma N_x M_x \tag{2.5}$$

Light scattering is an analytical method to determine the $\bar{M}_w$ in the range of 10,000–10,000,000. It unlike colligative properties shows a greater number for larger sized molecules than for small-sized molecules. Viscosity-average molecular weight ($\bar{M}_v$) is defined as Eq. 2.6, where a is a constant. The viscosity and

weight average molecular weights are equal when a is unity. $\bar{M}_v$ is like $\bar{M}_w$, it is greater for the larger sized polymer molecules than for smaller ones.

$$\bar{M}_v = \left[\Sigma\, M_x^a W_x\right]^{1/a} = \left[\Sigma\, N_x M_x^{a+1} / \Sigma N_x M_x\right]^{1/a} \tag{2.6}$$

A measure of the polydispersity in a polymer is defined as $\bar{M}_w$ divided over $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$). For a polydispersed polymer, $\bar{M}_w > \bar{M}_v > \bar{M}_n$ with the differences between the various average molecular weights increasing as the molecular-weight distribution (MWD) broadens, as shown in Fig. 2.2.

For example, consider a hypothetical mixture containing 95 % by weight of molecules of molecular weight 10,000, and 5 % of molecules of molecular weight 100. The $\bar{M}_n$ and $\bar{M}_w$ are calculated from Eqs. 2.1 and 2.2 as 1,680 and 9,505, respectively. The use of the $\bar{M}_n$ value of 1,680 gives an inaccurate indication of the properties of this polymer. The properties of the polymer are determined primarily by the molecules with a molecular weight of 10,000 that makes up 95 % of the weight of the mixture. The highest % fraction of molecular weight of molecule will contribute the most toward the bulk property. It is desirable to know the molecular weight distribution, then to predict the polymer properties. At present, the gel permeation chromatography (GPC) technique has been advanced to be able to easily measure $\bar{M}_n$, $\bar{M}_v$, $\bar{M}_w$, simultaneously and calculate PDI using only one sample. All the measurements of molecular weight of polymers are carried out using polymer solutions. Therefore, the accuracy of molecular weight measurement is dependent on the behavior of polymer solution. Usually, a calibration curve is established first using a specific polymer dissolving in a specific solvent. Polystyrene standard dissolved in tetrahydrofuran (THF) is the most popular calibration curve used in GPC. If the measured polymer exhibits different behavior in THF from that of polystyrene, then a deviation from the actual molecular weight is occurred. For example, a conducting polymer, poly (phenylene vinylene), containing rigid rod molecular structure shows a higher molecular weight when the standard of coil structured polystyrene is used. More detailed discussion of GPC is in Sect. 2.3.

Fig. 2.2 Distribution of molecular weights in a typical polymer sample [1]
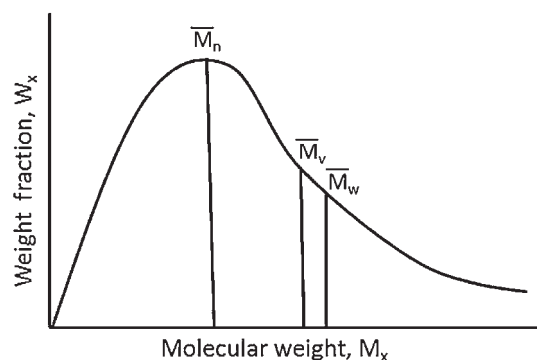
2.2 Polymer Solutions

Polymer solutions occur in two stages. Initially, the solvent molecules diffuse through the polymer matrix to form a swollen, solvated mass called a gel. In the second stage, the gel breaks up and the molecules are dispersed into a true solution. Not all polymers can form true solution in solvent.

Detailed studies of polymer solubility using thermodynamic principles have led to semi-empirical relationships for predicting the solubility [2]. Any solution process is governed by the free-energy relationship of Eq. 2.7:

$$\Delta G = \Delta H - T \Delta S \tag{2.7}$$

When a polymer dissolves spontaneously, the free energy of solution, ΔG, is negative. The entropy of solution, ΔS, has a positive value arising from increased conformational mobility of the polymer chains. Therefore, the magnitude of the enthalpy of solution, ΔH, determines the sign of ΔG. It has been proposed that the heat of mixing, ΔH_{mix}, for a binary system is related to concentration and energy parameters by Eq. 2.8:

$$\Delta H_{mix} = V_{mix} \left[\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 \emptyset_1 \emptyset_2 \tag{2.8}$$

where V_{mix} is the total volume of the mixture, V_1 and V_2 are molar volumes (molecular weight/density) of the two components, $\emptyset_1$ and $\emptyset_2$ are their volume fractions, and ΔE_1 and ΔE_2 are the energies of vaporization. The terms $\Delta E_1/V_1$ and $\Delta E_2/V_2$ are called the *cohesive energy densities.* If $(\Delta E/V)^{1/2}$ is replaced by the symbol δ, the equation can be simplified into Eq. 2.9:

$$\Delta H_{mix} = V_{mix} (\delta_1 - \delta_2)^2 \emptyset_1 \emptyset_2 \tag{2.9}$$

The interaction parameter between polymer and solvent can be estimated from ΔH_{mix} as:

$$\chi_{12} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \tag{2.10}$$

The symbol δ is called the solubility parameter. Clearly, for the polymer to dissolve (negative ΔG), ΔH_{mix} must be small; therefore, $(\delta_1 - \delta_2)^2$ must also be small. In other words, δ_1 and δ_2 should be of about equal magnitude where $\delta_1 = \delta_2$, solubility is governed solely by entropy effects. Predictions of solubility are therefore based on finding solvents and polymers with similar solubility parameters, which requires a means of determining cohesive energy densities.

Cohesive energy density is the energy needed to remove a molecule from its nearest neighbors, thus is analogous to the heat of vaporization per volume for a

volatile compound. For the solvent, δ_1 can be calculated directly from the latent heat of vaporization (ΔH_{vap}) using the relationship of Eq. 2.11:

$$\Delta E = \Delta H_{vap} - RT \qquad (2.11)$$

R is the gas constant, and T is the temperature in kelvins. Thus, the cohesive energy of solvent is shown in Eq. 2.12:

$$\delta_1 = \left(\frac{\Delta H_{vap} - RT}{V}\right)^{1/2} \qquad (2.12)$$

Since polymers have negligible vapor pressure, the most convenient method of determining δ_2 is to use group molar attraction constants. These are constants derived from studies of low-molecular-weight compounds that lead to numerical values for various molecular groupings on the basis of intermolecular forces. Two sets of values (designated G) have been suggested, one by Small [3], derived from heats of vaporization and the other by Hoy [4], based on vapor pressure measurements. Typical G values are given in Table 2.1. Clearly there are significant differences between the Small and Hoy values. The use of which set is normally determined by the method used to determine δ_1 for the solvent.

G values are additive for a given structure, and are related to δ by

$$\delta = \frac{d \Sigma G}{M} \qquad (2.13)$$

where d is density and M is molecular weight. For polystyrene $-[CH_2-CH(C_6H_5)]_n-$, for example, which has a density of 1.05, a repeating unit mass of 104, and δ is calculated, using Small's G values, as

Table 2.1 Representative group molar attraction constants [3, 4]

Chemical group	$G[(\text{cal cm}^3)^{1/2}\text{mol}^{-1}]$	
	Small	Hoy
H_3C-	214	147.3
$-CH_2-$	133	131.5
$>CH-$	28	86.0
$>C<$	−93	32.0
$=CH_2$	190	126.0
$=CH-$	19	84.5
$-C_6H_5$ (phenyl)	735	–
$-CH=$ (aromatic)	–	117.1
$>C=O$ (ketone)	275	262.7
$-CO_2-$ (ester)	310	326.6

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