# Chapter 2

# Physical and Thermal Analysis

## 2.1 Melting Point Analysis[1]

### 2.1.1 Introduction

Melting point (Mp) is a quick and easy analysis that may be used to qualitatively identify relatively pure samples (approximately <10% impurities). It is also possible to use this analysis to quantitatively determine purity. Melting point analysis, as the name suggests, characterizes the melting point, a stable physical property, of a sample in a straightforward manner, which can then be used to identify the sample.

### 2.1.2 Equipment

Although different designs of apparatus exist, they all have some sort of heating or heat transfer medium with a control, a thermometer, and often a backlight and magnifying lens to assist in observing melting (Figure 2.1). Most models today utilize capillary tubes containing the sample submerged in a heated oil bath. The sample is viewed with a simple magnifying lens. Some new models have digital thermometers and controls and even allow for programming. Programming allows more precise control over the starting temperature, ending temperature and the rate of change of the temperature.

[1] This content is available online at <http://cnx.org/content/m43565/1.1/>.

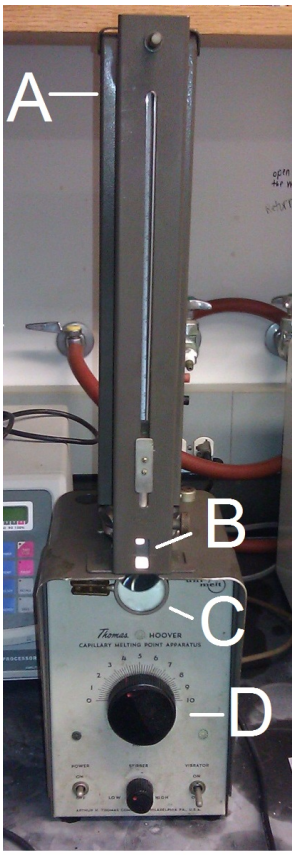


**Figure 2.1:** A Thomas Hoover melting point apparatus. The tower (A) contains a thermometer with a reflective view (B), so that the sample and temperature may be monitored simultaneously. The magnifying lens (C) allows better viewing of samples and lies above the heat controller (D).

### 2.1.3 Sample preparation

For melting point analysis, preparation is straight forward. The sample must be thoroughly dried and relatively pure ( <10% impurities). The dry sample should then be packed into a melting point analysis capillary tube, which is simply a glass capillary tube with only one open end. Only 1 to 3 mm of sample is needed for sufficient analysis. The sample needs to be packed down into the closed end of the tube. This may be done by gently tapping the tube or dropping it upright onto a hard surface (Figure 2.2). Some apparatuses have a vibrator to assist in packing the sample. Finally the tube should be placed into the machine. Some models can accommodate multiple samples.

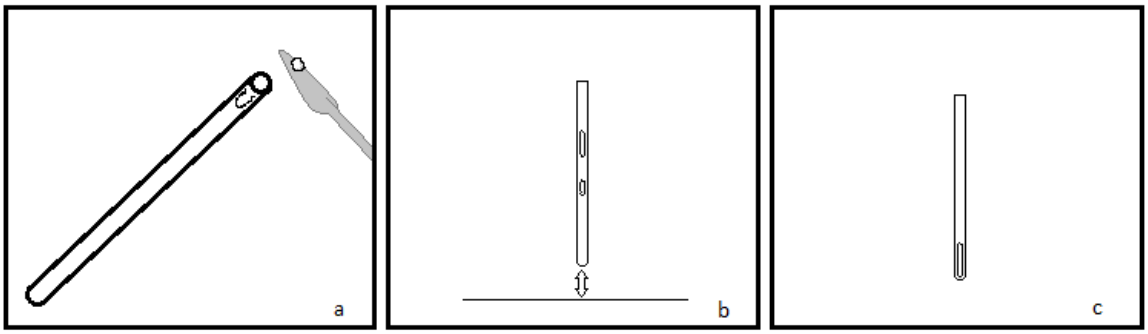


**Figure 2.2:** Schematic showing how to pack dried sample into a melting point analysis capillary tube: (a) using a spatula, push a sufficient amount of sample into the tube opening, (b) using a tapping motion or dropping the tube, pack the sample into the closed end, (c) the sample is ready to be loaded into the apparatus.

### 2.1.4 Recording data

Performing analysis is different from machine to machine, but the overall process is the same (Figure 2.3). If possible, choose a starting temperature, ending temperature, and rate of change of temperature. If the identity of the sample is known, base the starting and ending temperatures from the known melting point of the chemical, providing margins on both sides of the range. If using a model without programming, simply turn on the machine and monitor the rate of temperature change manually.

This media object is a Flash object. Please view or download it at
<http://www.youtube.com/v/9RNRYLvlbXM?version=3&hl=en_US>

**Figure 2.3:** A video discussing sample preparation, recording data and melting point analysis in general. Made by Indiana University-Purdue University Indianapolis chemistry department.

Visually inspect the sample as it heats. Once melting begins, note the temperature. When the sample is completely melted, note the temperature again. That is the melting point range for the sample. Pure samples typically have a 1 - 2 °C melting point range, however, this may be broadened due to colligative properties.

### 2.1.5 Interpreting data

There are two primary uses of melting point analysis data. The first is for qualitative identification of the sample, and the second is for quantitative purity characterization of the sample.

For identification, compare the experimental melting point range of the unknown to literature values. There are several vast databases of these values. Obtain a pure sample of the suspected chemical and mix a small amount of the unknown with it and conduct melting point analysis again. If a sharp melting point

range is observed at similar temperatures to the literature values, then the unknown has likely been identified correctly. Conversely, if the melting point range is depressed or broadened, which would be due to colligative properties, then the unknown was not successfully identified.

To characterize purity, first the identity of the solvent (the main constituent of the sample) and the identity of the primary solute need to be known. This may be done using other forms of analysis, such as gas chromatography-mass spectroscopy coupled with a database. Because melting point depression is unique between chemicals, a mixed melting curve comparing molar fractions of the two constituents with melting point needs to either be obtained or prepared (Figure 2.4). Simply prepare standards with known molar fraction ratios, then perform melting point analysis on each standard and plot the results. Compare the melting point range of the experimental sample to the curve to identify the approximate molar fractions of the constituents. This sort of purity characterization cannot be performed if there are more than two primary components to the sample.

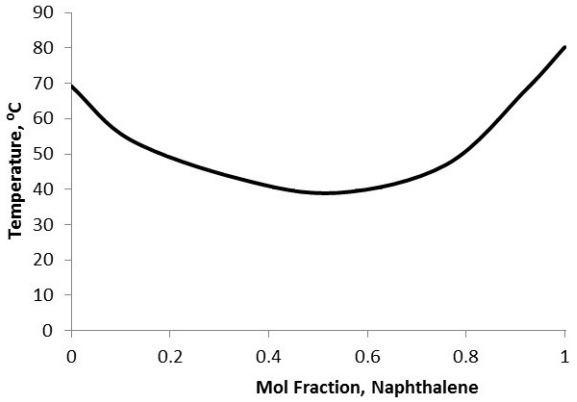


**Figure 2.4:** A mixed melting curve for naphthalene and biphenyl. Non-pure samples exhibit melting point depression due to colligative properties. Adapted from "Melting Point Analysis", Chem 211L, Clark College protocol.

## 2.1.6 Specificity and accuracy

Melting point analysis is fairly specific and accurate given its simplicity. Because melting point is a unique physical characteristic of a substance, melting point analysis does have high specificity. Although, many substances have similar melting points, so having an idea of possible chemicals in mind can greatly narrow down the choices. The thermometers used are also accurate. However, melting point is dependent on pressure as well, so experimental results can vary from literature values, especially at extreme locations, i.e., places of high altitude. The biggest source of error stems from the visual detection of melting by the experimenter. Controlling the change rate and running multiple trials can lessen the degree of error introduced at this step.

## 2.1.7 Advantages of melting point analysis

Melting point analysis is a quick, relatively easy, and inexpensive preliminary analysis if the sample is already mostly pure and has a suspected identity. Additionally, analysis requires small samples only.

### 2.1.8 Limitations of melting point analysis

As with any analysis, there are certain drawbacks to melting point analysis. If the sample is not solid, melting point analysis cannot be done. Also, analysis is destructive of the sample. For qualitative identification analysis, there are now more specific and accurate analyses that exist, although they are typically much more expensive. Also, samples with more than one solute cannot be analyzed quantitatively for purity.

### 2.1.9 Bibliography


- IUPUIORGANICCHEM, "Exp 3 Melting Point Determination", http://www.youtube.com/watch?v=9RNRYLvlbXM[2] , April 2012.
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- D. A. Straus, *Melting Point Analysis*, http://www.chemistry.sjsu.edu/straus/MP%20htms/MP1measure.htm[3] , April, 2012.
- *Thomas Hoover Melting Point Apparatus*, http://www.jce.divched.org/JCEsoft/CCA/CCA6/MAIN/1ChemLabMenu/ , April, 2012.


## 2.2 Molecular Weight Determination

### 2.2.1 Solution Molecular Weight of Small Molecules[5]

#### 2.2.1.1 Introduction

The cryoscopic method was formally introduced in the 1880's when François-Marie Raoult (Figure 2.5) published how solutes depressed the freezing points of various solvents such as benzene, water, and formic acid. He concluded from his experimentation "if one molecule of a substance can be dissolved in one-hundred molecules of any given solvent then the solvent temperature is lowered by a specific temperature increment". Based on Raoult's research, Ernst Otto Beckmann (Figure 2.6) invented the Beckmann thermometer and the associated freezing - point apparatus (Figure 2.7), which was a significant improvement in measuring freezing - point depression values for a pure solvent. The simplicity, ease, and accuracy of this apparatus has allowed it to remain as a current standard with few modifications for molecular weight determination of unknown compounds.

[2] http://www.youtube.com/watch?v=9RNRYLvlbXM
[3] http://www.chemistry.sjsu.edu/straus/MP%20htms/MP1measure.htm
[4] http://www.jce.divched.org/JCEsoft/CCA/CCA6/MAIN/1ChemLabMenu/Measuring/Temperature/meltpt_menu/meltpt_menu_4/MENU
[5] This content is available online at <http://cnx.org/content/m43553/1.1/>.

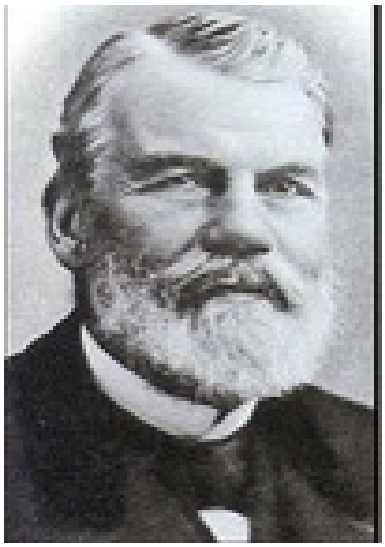

**Figure 2.5:** French chemist François-Marie Raoult (1830 - 1901).

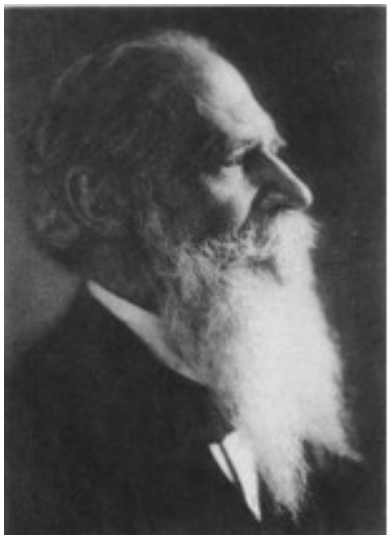

**Figure 2.6:** German chemist Ernst Otto Beckmann (1853 - 1923).

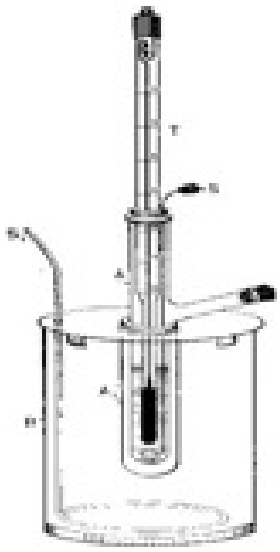

**Figure 2.7:** Beckmann differential thermometer and freezing point depression apparatus

The historical significance of Raoult and Beckmann's research, among many other investigators, has revolutionized a physical chemistry technique that is currently applied to a vast range of disciplines from food science to petroleum fluids. For example, measured cryoscopic molecular weights of crude oil are used to predict the viscosity and surface tension for necessary fluid flow calculations in pipeline.

#### 2.2.1.2 Freezing point depression

Freezing point depression is a colligative property in which the freezing temperature of a pure solvent decreases in proportion to the number of solute molecules dissolved in the solvent. The known mass of the added solute and the freezing point of the pure solvent information permit an accurate calculation of the molecular weight of the solute.

In (2.1) the freezing point depression of a non-ionic solution is described. Where $\Delta T_f$ is the change in the initial and final temperature of the pure solvent, $K_f$ is the freezing point depression constant for the pure solvent, and m (moles solute/kg solvent) is the molality of the solution.

$$\Delta T_f = K_f m \tag{2.1}$$

For an ionic solution shown in (2.2), the dissociation particles must be accounted for with the number of solute particles per formula unit, i (the van't Hoff factor).

$$\Delta T_f = K_f m i \tag{2.2}$$

#### 2.2.1.3 Cryoscopic procedure

##### 2.2.1.3.1 Cryoscopic apparatus

For cryoscopy, the apparatus to measure freezing point depression of a pure solvent may be representative of the Beckmann apparatus previously shown in Figure 2.7. The apparatus consists of a test tube containing

the solute dissolved in a pure solvent, stir bar or magnetic wire and closed with a rubber stopper encasing a mercury thermometer. The test tube component is immersed in an ice-water bath in a beaker. An example of the apparatus is shown in . The rubber stopper and stir bar/wire stirrer are not shown in the figure.

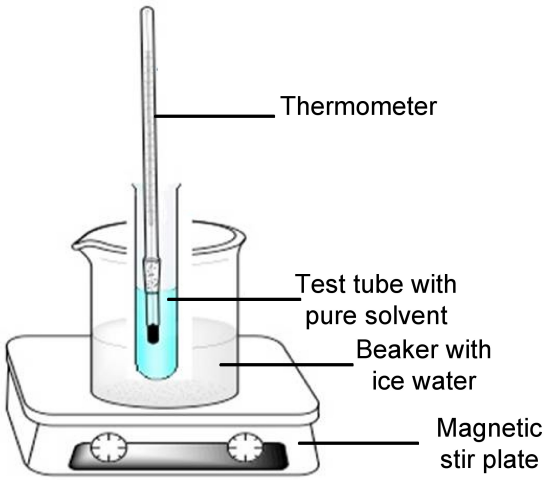


**Figure 2.8:** An example of a cryoscopic apparatus. Adapted from http://www.lahc.cc.ca.us/classes/chemistry/arias/Exp%2012%20-%20Freezing%20Point.pdf

#### 2.2.1.3.2 Sample and solvent selection

The cryoscopic method may be used for a wide range of samples with various degrees of polarity. The solute and solvent selection should follow the premise of like dissolved like or in terms of Raoult's principle of the dissolution of one molecule of solute in one-hundred molecules of a solvent. The most common solvents such as benzene are generally selected because it is unreactive, volatile, and miscible with many compounds. Table 2.1 shows the cryoscopic constants ($K_f$) for the common solvents used for cryoscopy. A complete list of $K_f$ values are available in Knovel Critical Tables.

| Compound | $K_f$ |
|---|---|
| Acetic Acid | 3.90 |
| Benzene | 5.12 |
| Camphor | 39.7 |
| Carbon disulfide | 3.8 |
| Carbon tetrachloride | 30 |
| Chloroform | 4.68 |
| Cyclohexane | 20.2 |
| Ethanol | 1.99 |
| Naphthalene | 6.80 |
| Phenol | 7.27 |
| Water | 1.86 |

**Table 2.1**: Cryoscopic constants ($K_f$) for common solvents used for cryoscopy.

#### 2.2.1.3.3 Cryoscopic Method

The detailed information about the procedure used for cryoscopy is shown below:

Step 1. Weigh (15 to 20 grams) of the pure solvent in a test tube and record the measured weight value of the pure solvent.
Step 2. Place a stir bar or wire stirrer in the test tube and close with a rubber stopper that has a hole to encase a mercury thermometer.
Step 3. Place a mercury thermometer in the rubber stopper hole.
Step 4. Immerse the test tube apparatus in an ice-water bath.
Step 5. Allow the solvent to stir continuously and equilibrate to a few degrees below the freezing point of the solvent.
Step 6. Record the temperature at which the solvent reaches the freezing point, which remains at a constant temperature reading.
Step 7. Repeat the freezing point data collection for at least two more measurements without a difference less than 0.5 °C between the measurements.
Step 8. Weigh a quantity of the solute for investigation and record the measured value.
Step 9. Add the weighed solute to the test tube containing the pure solvent.
Step 10. Re - close the test tube with a rubber stopper encasing a mercury thermometer.
Step 11. Re-immerse the test tube in an ice water bath and allow the mixture to stir to fully dissolve the solute in the pure solvent.
Step 12. Measure the freezing point and record the temperature value.

NOTE: Allow the solution to stir continuously to avoid supercooling.

The observed freezing point of the solution is when the temperature reading remains constant.

### 2.2.1.4 Sample calculation to determine molecular weight

#### 2.2.1.4.1 Sample data set

Table 2.2 represents an example of a data set collection for cryoscopy.

| Parameter | Trial 1 | Trial 2 | Trial 3 | Avg |
|---|---|---|---|---|
| Mass of cyclohexane (g) | 9.05 | 9.00 | 9.04 | 9.03 |
| Mass of unknown solute (g) | 0.4000 | 0.4101 | 0.4050 | 0.4050 |
| Freezing point of cyclohexane (°C) | 6.5 °C | 6.5 °C | 6.5 °C | 6.5 °C . |
| Freezing point of cyclohexane mixed with unknown solute (°C) | 4.2 °C | 4.3 °C | 4.2 °C | 4.2 °C |

**Table 2.2**: Example of a data set collection for cryoscopy

#### 2.2.1.4.2 Calculation of molecular weight using the freezing point depression equation

Calculate the freezing point (Fpt) depression of the solution,

$T\Delta_f$ (from Table 2.2).

$$T\Delta_f = \text{(Fpt of pure solvent) - (Fpt of solution)} \tag{2.3}$$

$$T\Delta_f = 6.5\ °C - 4.2\ °C \tag{2.4}$$

$$T\Delta_f = 2.3\ °C \tag{2.5}$$

Calculate the molal concentration, m, of the solution using the freezing point depression and $K_f$ (see Table 2.1 and Table 2.2).

$$T\Delta_f = K_f m \tag{2.6}$$

$$m = (2.3\ °C)/(20.2\ °C/molal) \tag{2.7}$$

$$m = 0.113\ molal \tag{2.8}$$

NOTE: $m = g\ (solute)/kg\ (solvent)$

Calculate the $M_W$ of the unknown sample.

NOTE: i = 1 for covalent compounds in (2.2).

$$M_W = \frac{K_f\ (g\ solute)}{\Delta T_f\ (kg\ solvent)} \tag{2.9}$$

$$M_W = \frac{20.2\ °C*kg/moles\ x\ 0.405\ g}{2.3\ °C\ x\ 0.00903\ kg} \tag{2.10}$$

$$M_W = 393\ g/mol \tag{2.11}$$

**Exercise 2.2.1.1** ***(Solution on p. 216.)***
Nicotine Figure 2.9 is an extracted pale yellow oil from tobacco leaves that dissolves in water at temperatures less than 60 °C. What is the molality of nicotine in an aqueous solution that begins to freeze at -0.445 °C? See Table 2.1 for $K_f$ values.

**Exercise 2.2.1.2** ***(Solution on p. 216.)***
If the solution used in Exercise 2.2.1.1 is obtained by dissolving 1.200 g of nicotine in 30.56 g of water, what is the molar mass of nicotine?

**Exercise 2.2.1.3** ***(Solution on p. 216.)***
What would be the freezing point depression when 0.500 molal of $Ca(NO_3)_2$ is dissolved in 60 g of water?

**Exercise 2.2.1.4** ***(Solution on p. 216.)***
Calculate the number of weighed grams of $Ca(NO_3)_2$ added to the 60 g of water to achieve the freezing point depression from Exercise 2.2.1.3? The $M_W$ of $Ca(NO_3)_2$ is 164.088 g/moles.

#### 2.2.1.5 Bibliography


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### 2.2.2 Molecular Weight of Polymers[6]

#### 2.2.2.1 Introduction

Knowledge of the molecular weight of polymers is very important because the physical properties of macromolecules are affected by their molecular weight. For example, shown in Figure 2.10 the interrelation between molecular weight and strength for a typical polymer.

[6] This content is available online at <http://cnx.org/content/m43550/1.1/>.

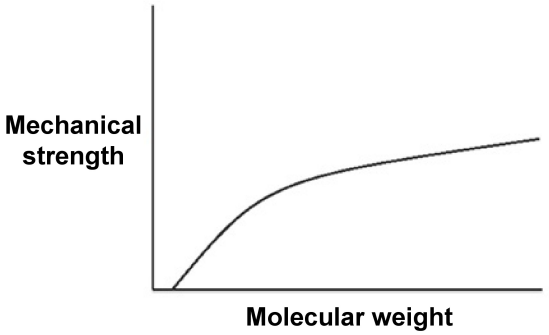


**Figure 2.10:** Dependence of mechanical strength on polymer molecular weight. Adapted from G. Odian, *Principles of Polymerization,* $4^{\text{th}}$ edition, Willey-Interscience, New York (2004).

The melting point of polymers are also slightly depend on their molecular weight. (Figure 2.11) shows relationship between molecular weight and melting temperatures of polyethylene (Figure 2.12). Most linear polyethylenes have melting temperatures near 140 °C. The approach to the theoretical asymptote, that is a line whose distance to a given curve tends to zero, indicative that a theoretical polyethylene of infinite molecular weight (i.e., $M = \infty$) would have a melting point of 145 °C.

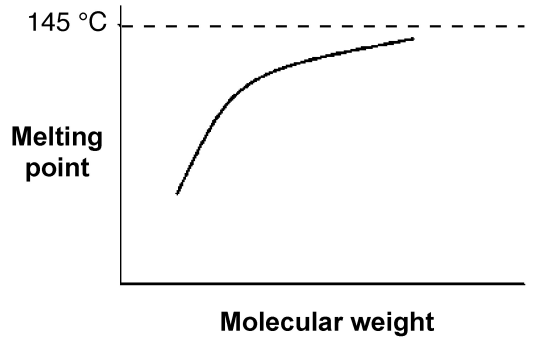


**Figure 2.11:** The molecular weight-melting temperature relationship for the alkane series. Adapted from L. H. Sperling, *Introduction to physical polymer science,* $4^{\text{th}}$ edition, Wiley-Interscience, New York (2005).

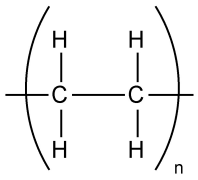


**Figure 2.12:** Structure of polyethylene.

There are several ways to calculate molecular weight of polymers like number average of molecular weight, weight average of molecular weight, Z-average molecular weight, viscosity average molecular weight, and distribution of molecular weight.

### 2.2.2.2 Molecular weight of polymers

#### 2.2.2.2.1 Number average of molecular weight ($M_n$)

Number average of molecular weight is measured to determine number of particles. Number average of molecular weight is the total weight of polymer, (2.12), divided by the number of polymer molecules, (2.13). The number average molecular weight ($M_n$) is given by (2.14), where $M_i$ is molecular weight of a molecule of oligomer n, and $N_i$ is number of molecules of that molecular weight.

$$\text{Total weight} = \Sigma_{i=1}^{\infty} M_i N_i \tag{2.12}$$

$$\text{Total number} = \Sigma_{i=1}^{\infty} N_i \tag{2.13}$$

$$M_n = \frac{\Sigma M_i N_i}{\Sigma N_i} \tag{2.14}$$

**Example 2.1**
Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 40.000 g/mol and 15 moles of polymer molecules having molecular weight of 30.000 g/mol.

$$\text{Total weight} = (5 \text{ mol x } 40.00 \text{ g/mol}) + (15 \text{ mole x } 30.00 \text{ g/mol}) = 650{,}000 \text{ g} \tag{2.15}$$

$$\text{Total number} = 5 \text{ mol} + 15 \text{ mol} = 20 \text{ mol} \tag{2.16}$$

$$M_n = \frac{650{,}000 \text{ g}}{20 \text{ mol}} = 325{,}000 \text{ g/mol} \tag{2.17}$$

#### 2.2.2.2.2 Weight average of molecular weight ($M_w$)

Weight average of molecular weight ($M_w$) is measured to determine the mass of particles. $M_w$ defined as (2.18), where $M_i$ is molecular weight of a molecule of oligomer n, and $N_i$ is number of molecules of that molecular weight.

$$M_W = \frac{\Sigma N_i (M_i)^2}{\Sigma N_i M_i} \tag{2.18}$$

**Example 2.2**

Consider the polymer described in Example 2.1.

$$M_W = \frac{(5 \text{ mol x } (40{,}000 \text{ g/mol})^2) + (15 \text{ mol x } (30{,}000 \text{ g/mol})^2)}{(5 \text{ mol x } 40{,}000 \text{ g/mol}) + (15 \text{ mol x } 30{,}000 \text{ g/mol})} \tag{2.19}$$

$$M_W = 330{,}769 \text{ g/mol} \tag{2.20}$$

**Exercise 2.2.2.1** *(Solution on p. 216.)*

Calculate the $M_W$ for a polymer sample comprising of 9 moles of polymer molecules having molecular weight of 30.000 g/mol and 5 moles of polymer molecules having molecular weight of 50.000 g/mol.

#### 2.2.2.2.3 Z-average molecular weight ($M_z$)

The Z-average molecular weight ($M_z$) is measured in some sedimentation equilibrium experiments. $M_z$ isn't common technique for molecular weight of polymers. The molar mass depends on size and mass of the molecules. The ultra centrifugation techniques employ to determine $M_z$. $M_z$ emphasizes large particles and it defines the EQ, where $M_i$ is molecular weight and $N_i$ is number of molecules.

$$M_W = \frac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2} \tag{2.21}$$

**Example 2.3**

Consider the polymer described in Example 2.1.

$$M_Z = \frac{(5 \text{ mol x } (40{,}000 \text{ g/mol})^3) + (15 \text{ mol x } (30{,}000 \text{ g/mol})^3)}{(5 \text{ mol x } (40{,}000 \text{ g/mol})^2) + (15 \text{ mol x } (30{,}000 \text{ g/mol})^2)} \tag{2.22}$$

$$M_Z = \frac{7.25 \text{ x } 10^{14} \text{ g}^3/\text{mol}^4}{2.15 \text{ x } 10^{10} \text{ g}^2/\text{mol}^3} \tag{2.23}$$

$$M_Z = 337{,}209 \text{ g/mol} \tag{2.24}$$

**Exercise 2.2.2.2** *(Solution on p. 216.)*

Calculate the $M_Z$ for a polymer sample comprising of 10 moles of polymer molecules having molecular weight of 20.000 g/mol and 2 moles of polymer molecules having molecular weight of 25,000 g/mol.

#### 2.2.2.2.4 Viscosity average molecular weight ($M_v$)

One of the ways to measure the average molecular weight of polymers is viscosity of solution. Viscosity of a polymer depend on concentration and molecular weight of polymers. Viscosity techniques is common since it is experimentally simple. Viscosity average molecular weight defines as (2.25), where $M_i$ is molecular weight and $N_i$ is number of molecules, a is a constant which depend on the polymer-solvent in the viscosity experiments. When a is equal 1, $M_v$ is equal to the weight average molecular weight, if it isn't equal 1 it is between weight average molecular weight and the number average molecular weight.

$$M_V = \left( \frac{\Sigma N_i M_i^{1+a}}{\Sigma N_i M_i} \right)^{1/2} \tag{2.25}$$

#### 2.2.2.2.5 Distribution of molecular weight

Molecular weight distribution is one of the important characteristic of polymer because it affects polymer properties. A typical molecular distribution of polymers show in Figure 2.13.. There are various molecular weight in the range of curve. The distribution of sizes in a polymer sample isn't totally defined by its central tendency. The width and shape of distribution must be known. It is always true that the various range molecular weight is (2.26). The equality is occurring when all polymer in the sample have the same molecular weight.

$$M_N \leq M_V \leq M_W \leq M_Z \leq M_{Z+1} \tag{2.26}$$

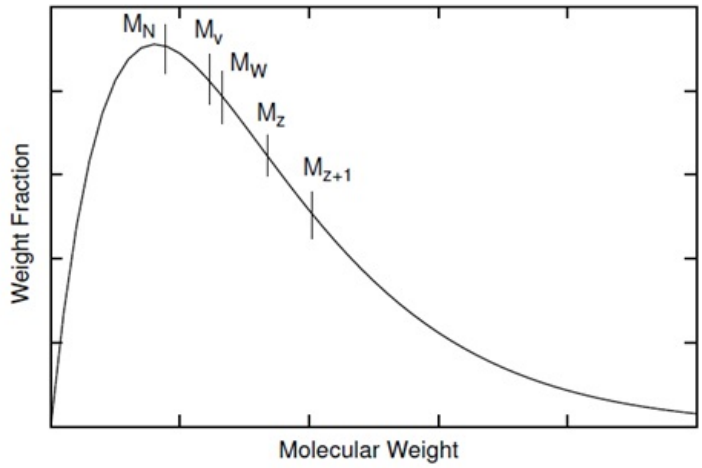


**Figure 2.13:** A schematic plot of a distribution of molecular weights along with the rankings of the various average molecular weights. Adapted from J. A. Nairn, Oregon State University (2003).

### 2.2.2.3 Molecular weight analysis of polymers

#### 2.2.2.3.1 Gel permeation chromatography (GPC)

Gel permeation chromatography is also called size exclusion chromatography. It is widely used method to determine high molecular weight distribution. In this technique, substances separate according to their molecule size. Firstly, large molecules begin to elute then smaller molecules are eluted Figure 2.14. The sample is injected into the mobile phase then the mobile phase enters into the columns. Retention time is the length of time that a particular fraction remains in the column. As shown in Figure 2.14, while the mobile phase passes through the porous particles, the area between large molecules and small molecules is getting increase. GPC gives a full molecular distribution, but its cost is high.

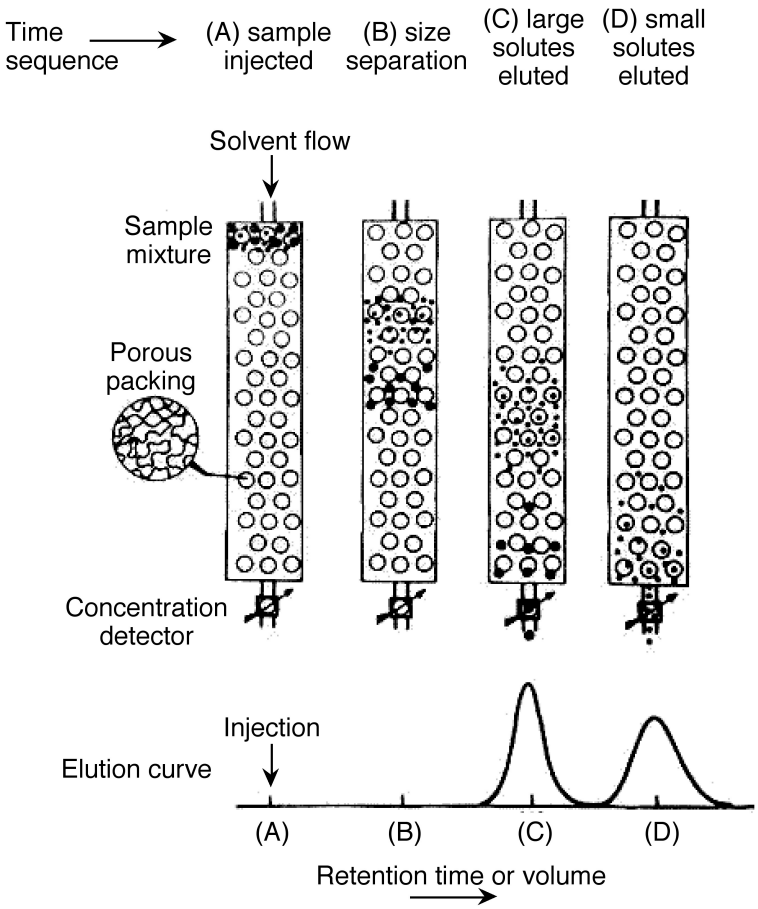


**Figure 2.14:** Solvent flow through column. Adapted from A. M. Striegel, W. W. Yau, J. J. Kirkland, and D. D. Bly. *Modern Size-Exclusion Liquid Chromatography- Practice of Gel Permeation and Gel Filtration Chromatography*, 2nd Edition. Hoboken. N.J. (2009).

According to basic theory of GPC, the basic quantity measured in chromatography is the retention volume, (2.27), where $V_0$ is mobile phase volume and $V_p$ is the volume of a stationary phase. K is a

distribution coefficient related to the size and types of the molecules.

$$V_e = V_0 + V_p K \tag{2.27}$$

The essential features of gel permeation chromatography are shown in Figure 2.15. Solvent leaves the solvent supply, then solvent is pumped through a filter. The desired amount of flow through the sample column is adjusted by sample control valves and the reference flow is adjusted that the flow through the reference and flow through the sample column reach the dedector in common front. The reference column is used to remove any slight impurities in the solvent. In order to determine the amount of sample, a detector is located at the end of the column. Also, detectors may be used to continuously verify the molecular weight of species eluting from the column. The flow of solvent volume is as well monitored to provide a means of characterizing the molecular size of the eluting species.

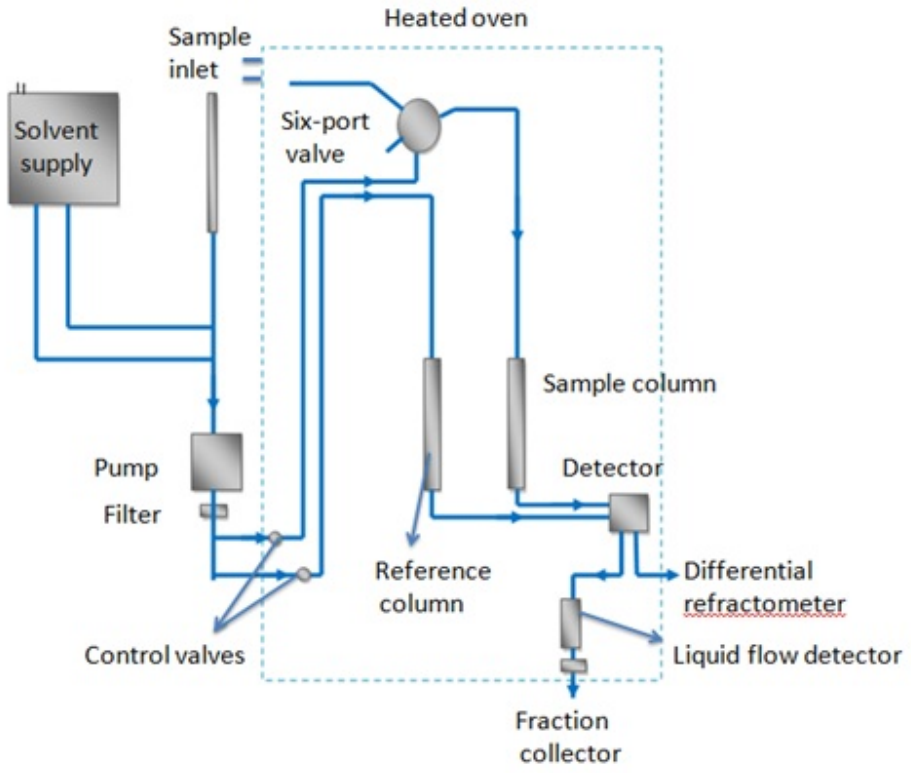


**Figure 2.15:** Schematic of gel permeation chromatography system.

As an example, consider the block copolymer of ethylene glycol (PEG, Figure 2.19) and poly(lactide) (PLA, Figure 2.17), i.e., Figure 2.18. In the first step starting with a sample of PEG with a $M_n$ of 5,700 g/mol. After polymerization, the molecular weight increased because of the progress of lactide polymerization initiated from end of PEG chain. Varying composition of PEG-PLA shown in Table 2.3 can be detected by GPC (Figure 2.19).

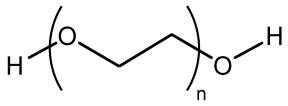


**Figure 2.16:** The structure of polyethyleneglycol (PEG).

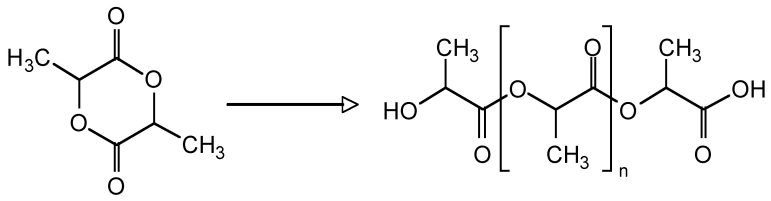


**Figure 2.17:** The ring-opening polymerization of lactide to polylactide.

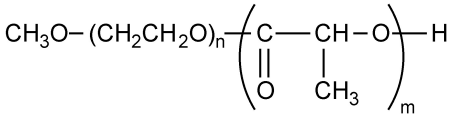


**Figure 2.18:** The structure of PEG-PLA block copolymer.

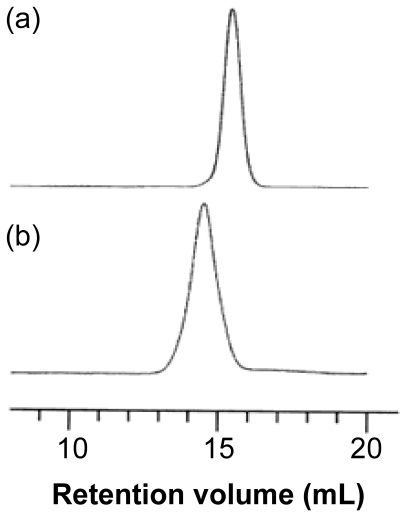


**Figure 2.19:** Gel permeation chromatogram of (a) PEG ($M_W$ = 5,700 g/mol) and (b) PEG-PLA block copolymer ($M_W$ = 11,000 g/mol). Adapted from K. Yasugi, Y. Nagasaki, M. Kato, K. Kataoka, *J. Control. Release*, 1999, **62,** 89.

| **Polymer** | **$M_n$ of PEG** | **$M_w/M_n$ of PEG** | **$M_n$ of PLA** | **$M_w$ /$M_n$ of block copolymer** | **Weight ratio of PLA to PEG** |
|---|---|---|---|---|---|
| PEG-PLA(41-12) | 4100 | 1.05 | 1200 | 1.05 | 0.29 |
| PEG-PLA(60-30) | 6000 | 1.03 | 3000 | 1.08 | 0.50 |
| PEG-PLA(57-54) | 5700 | 1.03 | 5400 | 1.08 | 0.95 |
| PEG-PLA(61-78) | 6100 | 1.03 | 7800 | 1.11 | 1.28 |

**Table 2.3**: Characteristics of PEG-PLA block copolymer with varying composition. Adapted from K. Yasugi, Y. Nagasaki, M. Kato, and K. Kataoka, *J. Control Release*, 1999, **62**, 89.

#### 2.2.2.3.2 Light-scattering

One of the most used methods to characterize the molecular weight is light scattering method. When polarizable particles are placed in the oscillating electric field of a beam of light, the light scattering occurs. Light scattering method depends on the light, when the light is passing through polymer solution, it is measure by loses energy because of absorption, conversion to heat and scattering. The intensity of scattered light relies on the concentration, size and polarizability that is proportionality constant which depends on the molecular weight. Figure 2.20 shows light scattering off a particle in solution.

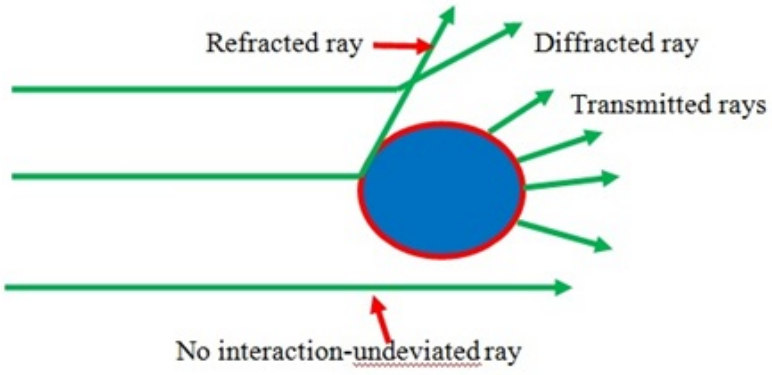


**Figure 2.20:** Modes of scattering of light in solution.

A schematic laser light-scattering is shown in Figure 2.21. A major problem of light scattering is to prepare perfectly clear solutions. This problem is usually accomplished by ultra-centrifugation. A solution should be as possible as clear and dust free to determine absolute molecular weight of polymer. The advantages of this method, it doesn't need calibration to obtain absolute molecular weight and it can give information about shape and $M_w$ information. Also, it can be performed rapidly with less amount of sample and absolute determinations of the molecular weight can be measured. The weaknesses of the method is high price and most times it requires difficult clarification of the solutions.

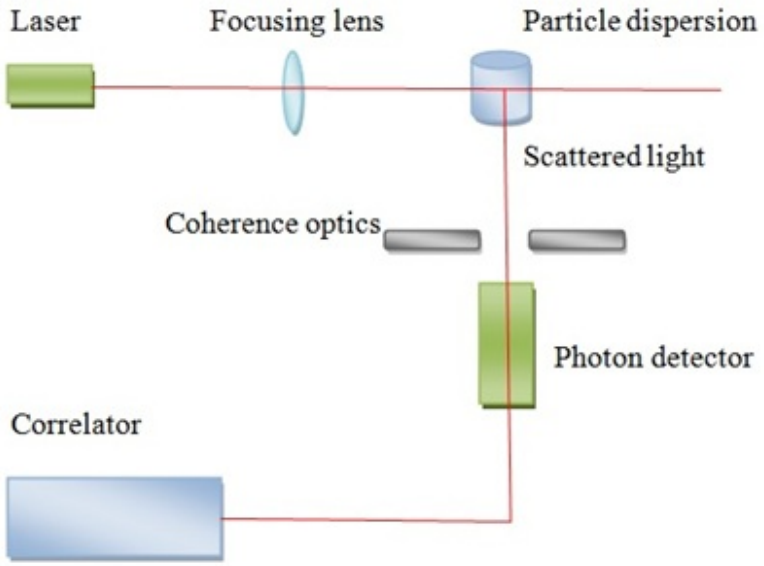


**Figure 2.21:** Schematic representation of light scattering. Adapted from J. A. Nairn, polymer characterization, *Material science and engineering 5473*, spring 2003.

The weight average molecular weight value of scattering polymers in solution related to their light scattering properties that define by (2.28), where K is the wave vector, that defined by (2.29). C is solution concentration, $R(\theta)$ is the reduced Rayleigh ratio, $P(\theta)$ the particle scattering function, $\theta$ is the scattering angle, A is the osmotic virial coefficients, where $n_0$ solvent refractive index, $\lambda$ the light wavelength and $N_a$ Avagadro's number. The particle scattering function is given by (2.30), where $R_z$ is the radius of gyration.

$$KC/R(\theta) = 1/ M_w(P(\theta) + 2A_2C + 3A_3C_2 + \ldots) \tag{2.28}$$

$$K = 2\pi^2 n_0^2 (dn/dC)^2 / N_a \lambda^4 \tag{2.29}$$

$$1/(P(\theta) = 1+16\pi^2 n_0^2 (R_z^2) \sin^2(\theta/2) 3\lambda^2 \tag{2.30}$$

Weight average molecular weight of a polymer is found from extrapolation of data in the form of a Zimm plot (Figure 2.22). Experiments are performed at several angles and at least at 4 different concentrations. The straight line extrapolations provides $M_w$.

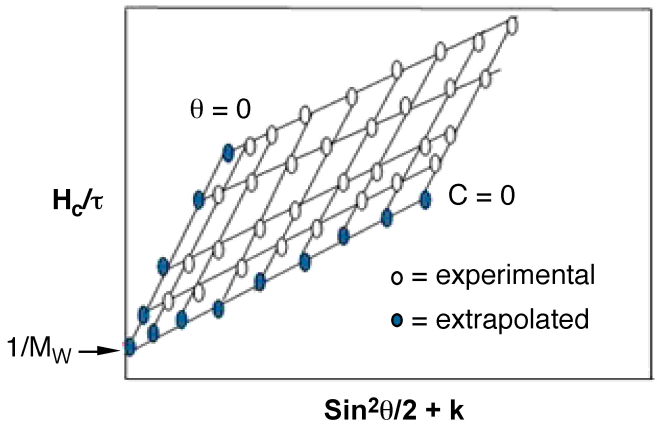


**Figure 2.22:** A typical Zimm plot of light scattering data. Adapted from M. P. Stevens, *Polymer Chemistry an Introduction*, 3rd edition, Oxford University Press, Oxford (1999).

#### 2.2.2.3.3 X-ray scattering

X-rays are a form of electromagnetic wave with wavelengths between 0.001 nm and 0.2 nm. X-ray scattering is particularly used for semicrystalline polymers which includes thermoplastics, thermoplastic elastomers, and liquid crystalline polymers. Two types of X-ray scattering are used for polymer studies:

1. Wide-angle X-ray scattering (WAXS) which is used to study orientation of the crystals and the packing of the chains.
2. Small-angle X-ray scattering (SAXS) which is used to study the electron density fluctuations that occur over larger distances as a result of structural inhomogeneities.

Schematic representation of X-ray scattering shows in Figure 2.23.

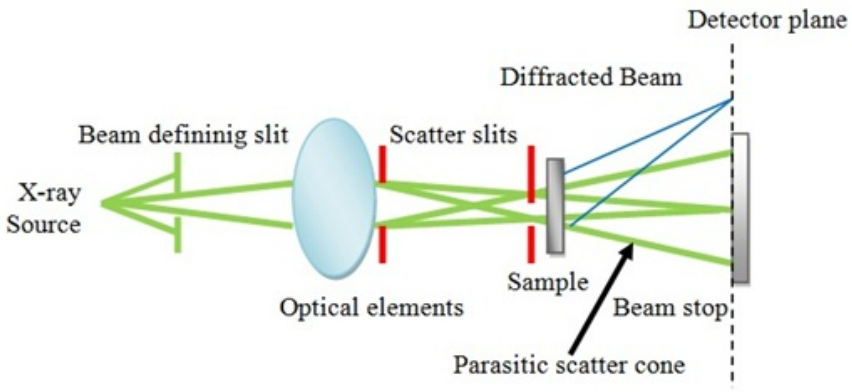


**Figure 2.23:** Schematic diagram of X-ray scattering. Adapted from B. Chu, and B. S. Hsiao, *Chem. Rev.* 2001,**101**, 1727.

At least two SAXS curves are required to determine the molecular weight of a polymer. The SAXS procedure to determine the molecular weight of polymer sample in monomeric or multimeric state solution requires the following conditions.

a. The system should be monodispersed.
b. The solution should be dilute enough to avoid spatial correlation effects.
c. The solution should be isotropic.
d. The polymer should be homogeneous.

#### 2.2.2.3.4 Osmometer

Osmometry is applied to determine number average of molecular weight ($M_n$). There are two types of osmometer:

1. Vapor pressure osmometry (VPO).
2. Membrane osmometry.

Vapor pressure osmometry measures vapor pressure indirectly by measuring the change in temperature of a polymer solution on dilution by solvent vapor and is generally useful for polymers with $M_n$ below 10,000–40,000 g/mol. When molecular weight is more than that limit, the quantity being measured becomes very small to detect. A typical vapor osmometry shows in the Figure 2.24. Vapor pressure is very sensitive because of this reason it is measured indirectly by using thermistors to measure voltage changes caused by changes in termperature.

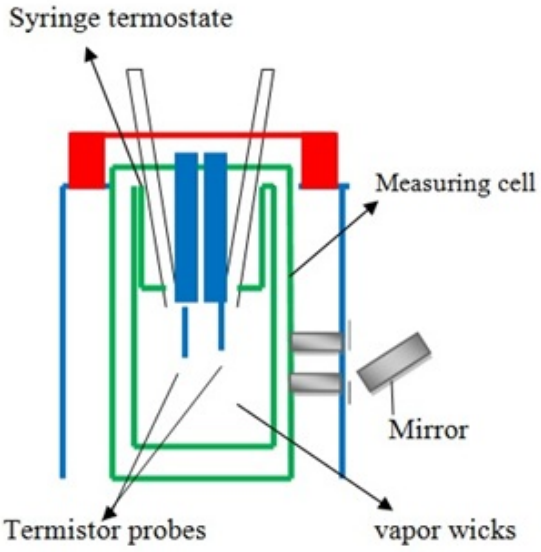


**Figure 2.24:** Schematic vapor pressure osmometry. Adapted from http://www.gallay.com.au/node/186[7]

Membrane osmometry is absolute technique to determine $M_n$ (Figure 2.25). The solvent is separated from the polymer solution with semipermeable membrane that is strongly held between the two chambers. One chamber is sealed by a valve with a transducer attached to a thin stainless steel diaphragm which permits the measurement of pressure in the chamber continuously. Membrane osmometry is useful to determine $M_n$ about 20,000-30,000 g/mol and less than 500,000 g/mol. When $M_n$ of polymer sample more than 500,000 g/mol, the osmotic pressure of polymer solution becomes very small to measure absolute number average of molecular weight. In this technique, there are problems with membrane leakage and symmetry. The advantages of this technique is that it doesn't require calibration and it gives an absolute value of $M_n$ for polymer samples.

[7] http://www.gallay.com.au/node/186

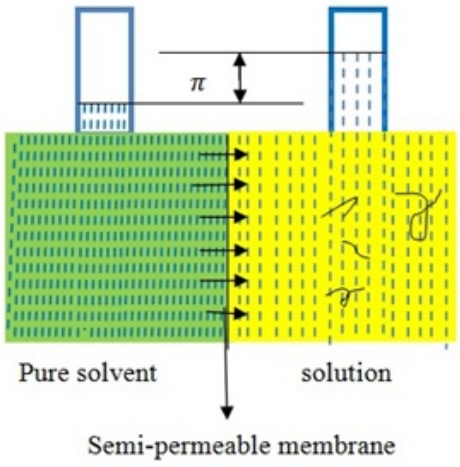


**Figure 2.25:** Schematic representative of membrane osmometry. Adapted from http://www.flickr.com/photos/mitopencourseware/3327963527/[8].

#### 2.2.2.4 Summary

Properties of polymers depend on their molecular weight. There are different kind of molecular weight and each can be measured by different techniques. The summary of these techniques and molecular weight is shown in the Table 2.4.

| Method | Type of molecular weight | Range of application |
|---|---|---|
| Light scattering | $M_w$ | $\infty$ |
| Membrane osmometry | $M_n$ | $10^4$-$10^6$ |
| Vapor phase osmometry | $M_n$ | 40,000 |
| X-ray scattering | $M_{w,\ n,\ z}$ | $10^2$ to |

**Table 2.4**: Summary of techniques of molecular weight of polymers.

#### 2.2.2.5 Bibliography


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- http://www.flickr.com/photos/mitopencourseware/3327963527/ [10]


## 2.2.3 Size Exclusion Chromatography and its Application in Polymer Science[11]

### 2.2.3.1 Introduction

Size exclusion chromatography (SEC) is a useful technique that is specifically applicable to high-molecular-weight species, such as polymer. It is a method to sort molecules according to their sizes in solution. The sample solution is injected into the column, which is filled with rigid, porous, materials, and is carried by the solvent through the packed column. The sizes of molecules are determined by the pore size of the packing particle in the column within which the separation occurs.

For polymeric materials, the molecular weight ($M_w$) or molecular size plays a key role in determining the mechanical, bulk, and solution properties of materials. It is known that the sizes of polymeric molecules depend on their molecular weights, side chain configurations, molecular interaction, and so on. For example, the exclusion volume of polymers with rigid side group is larger than those with soft long side chains. Therefore, in order to determine the molecular weight and molecular weight distribution of a polymer, one of the most widely applied methods is gel-permeation chromatography.

> NOTE: Gel permeation chromatography (GPC) is a term used for when the separation technique size exclusion chromatography (SEC) is applied to polymers.

The primary purpose and use of the SEC technique is to provide molecular weight distribution information about a particular polymeric material. Typically, in about 30 minutes using standard SEC, the complete molecular weight distribution of a polymer as well as all the statistical information of the distribution can be determined. Thus, SEC has been considered as a technique essentially supplanting classical molecular weight techniques. To apply this powerful technique, there is some basic work that needs to be done before its use. The selection of an appropriate solvent and the column, as well as the experimental conditions, are important for proper separation of a sample. Also, it is necessary to have calibration curves in order to determine the relative molecular weight from a given retention volume/time.

It is well known that both the majority of natural and synthetic polymers are polydispersed with respect to molar mass. For synthetic polymers, the more mono-dispersed a polymer can be made, the better the understanding of its inherent properties will be obtained.

### 2.2.3.2 Polymer properties

A polymer is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. Polymers are common materials that are widely used in our lives. One of the most important features which distinguishes most synthetic polymers from simple molecular compounds is the inability to assign an exact molar mass to a polymer. This is a consequence of the fact that during

[9] http://www.gallay.com.au/node/186
[10] http://www.flickr.com/photos/mitopencourseware/3327963527/
[11] This content is available online at <http://cnx.org/content/m34657/1.2/>.

the polymerization reaction the length of the chain formed is determined by several different events, each of which have different reaction rates. Hence, the product is a mixture of chains of different length due to the random nature of growth. In addition, some polymers are also branched (rather than linear) as a consequence of alternative reaction steps. The molecular weight ($M_w$) and molecular weight distribution influences many of the properties of polymers:

- **Processability** - the suitability of the polymer to physical processing.
- **Glass-transition temperature** - refers to the transformation of a glass-forming liquid into a glass.
- **Solution viscosity** - measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress.
- **Hardness** - a measure of how resistant a polymer is to various kinds of permanent shape change when a force is applied.
- **Melt viscosity** - the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load.
- **Tear strength** - a measure of the polymers resistance to tearing.
- **Tensile strength** - as indicated by the maxima of a stress-strain curve and, in general, is the point when necking occurs upon stretching a sample.
- **Stress-crack resistance** - the formation of cracks in a polymer caused by relatively low tensile stress and environmental conditions.
- **Brittleness** - the liability of a polymer to fracture when subjected to stress.
- **Impact resistance** - the relative susceptibility of polymers to fracture under stresses applied at high speeds.
- **Flex life** - the number of cycles required to produce a specified failure in a specimen flexed in a prescribed manner.
- **Stress relaxation** - describes how polymers relieve stress under constant strain.
- **Toughness** - the resistance to fracture of a polymer when stressed.
- **Creep strain** - the tendency of a polymer to slowly move or deform permanently under the influence of stresses.
- **Drawability** - The ability of fiber-forming polymers to undergo several hundred percent permanent deformation, under load, at ambient or elevated temperatures.
- **Compression** - the result of the subjection of a polymer to compressive stress.
- **Fatigue** - the failure by repeated stress.
- **Tackiness** - the property of a polymer being adhesive or gummy to the touch.
- **Wear** - the erosion of material from the polymer by the action of another surface.
- **Gas permeability** - the permeability of gas through the polymer.

Consequently, it is important to understand how to determine the molecular weight and molecular weight distribution.

#### 2.2.3.2.1 Molecular weight

Simpler pure compounds contain the same molecular composition for the same species. For example, the molecular weight of any sample of styrene will be the same (104.16 g/mol). In contrast, most polymers are not composed of identical molecules. The molecular weight of a polymer is determined by the chemical structure of the monomer units, the lengths of the chains and the extent to which the chains are interconnected to form branched molecules. Because virtually all polymers are mixtures of many large molecules, we have to resort to averages to describe polymer molecular weight.

The polymers produced in polymerization reactions have lengths which are distributed according to a probability function which is governed by the polymerization reaction. To define a particular polymer weight average, the average molecular weight $M_{avg}$ is defined by (2.31). Where $N_i$ is the number of molecules with

molecular weight $M_i$.

$$M_{avg} = \frac{\sum N_i M_i^a}{\sum N_i M_i^{a-1}} \tag{2.31}$$

There are several possible ways of reporting polymer molecular weight. Three commonly used molecular weight descriptions are: the number average ($M_n$), weight average ($M_w$), and z-average molecular weight ($M_z$). All of three are applicable to different constant a in (2.31) and are shown in Figure 2.26.

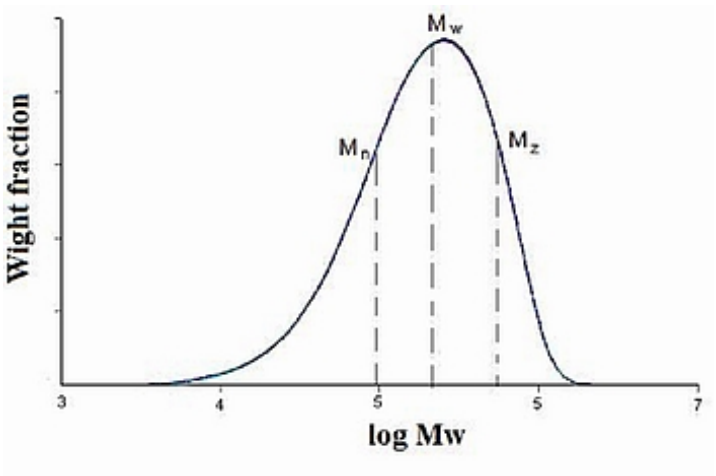


**Figure 2.26:** Distribution of molar masses for a polymer sample.

When a = 1, the number average molecular weight, (2.32).

$$M_{n,avg} = \frac{\sum N_i M_i}{\sum N_i} = \frac{w}{N} \tag{2.32}$$

When a = 2, the weight average molecular weight, (2.33).

$$M_{w,avg} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum N_i M_i}{w} \tag{2.33}$$

When a = 3, the z-average average molecular weight, (2.34).

$$M_{z,avg} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2.34}$$

Bulk properties weight average molecular weight, $M_w$ is the most useful one, because it fairly accounts for the contributions of different sized chains to the overall behavior of the polymer, and correlates best with most of the physical properties of interest.

There are various methods published to detect these three different primary average molecular weights respectively. For instance, a colligative method, such as osmotic pressure, effectively calculates the number

of molecules present and provides a number average molecular weight regardless of their shape or size of polymers. The classical van't Hoff equation for the osmotic pressure of an ideal, dilute solution is shown in (2.35).

$$\frac{\pi}{c} = \frac{RT}{M_n} \tag{2.35}$$

The weight average molecular weight of a polymer in solution can be determined by either measuring the intensity of light scattered by the solution or studying the sedimentation of the solute in an ultracentrifuge. From light scattering method which is depending on the size rather than the number of molecules, weight average molecular weight is obtained. This work requires concentration fluctuations which are the main source of the light scattered by a polymer solution. The intensity of the light scattering of polymer solution is often expressed by its turbidity $\tau$ which is given in *Rayleigh's law* in (2.36). Where $i_\theta$ is scattered intensity at only one angle $\theta$, r is the distance from the scattering particle to the detection point, and $I_0$ is the incident intensity.

$$\tau = \frac{16\pi i_\theta r^2}{3I_0(1+\cos^2\theta)} \tag{2.36}$$

The intensity scattered by molecules ($N_i$) of molecular weight ($M_i$) is proportional to $N_iM_i^2$. Thus, the total light scattered by all molecules is described in (2.37), where c is the total weight of the sample $\sum N_iM_i$.

$$\frac{\pi}{c} \sim \frac{\sum N_iM_i^2}{\sum N_iM_i} = M_{w,\,avg} \tag{2.37}$$

#### 2.2.3.2.2 Poly-disperse index (PDI)

The polydispersity index (PDI), is a measure of the distribution of molecular mass in a given polymer sample. As shown in Figure 2.26, it is the result of the definitions that $M_w \geq M_n$. The equality of $M_w$ and $M_n$ would correspond with a perfectly uniform (monodisperse) sample. The ratio of these average molecular weights is often used as a guide to the dispersity of the chain lengths in a polymer sample. The greater $M_w$ / $M_n$ is, the greater the dispersity is.

The properties of a polymer sample are strongly dependent on the way in which the weights of the individual molecules are distributed about the average. The ratio $M_w/M_n$ gives sufficient information to characterize the distribution when the mathematical form of the distribution curve is known.

Generally, the narrow molecular weight distribution materials are the models for much of work aimed at understanding the materials' behaviors. For example, polystyrene and its block copolymer polystyrene-b-polyisoprene have quite narrow distribution. As a result, narrow molecular weight distribution materials are a necessary requirement when people study their behavior, such as self-assembly behavior for block copolymer. Nonetheless, there are still lots of questions for scientists to explore the influence of polydispersity. For example, research on self-assembly which is one of the interesting fields in polymer science shows that we cannot throw polydispersity away.

#### 2.2.3.3 Setup of SEC equipment

In SEC, sample components migrate through the column at different velocities and elute separately from the column at different times. In liquid chromatography and gas chromatography, as a solute moves along with the carrier fluid, it is at times held back either by surface of the column packing, by stationary phase, or by both. Unlike gas chromatography (GC) and liquid chromatography (LC), molecular size, or more precisely, molecular hydrodynamic volume governs the separation process of SEC, not varied by the type of mobile

phase. The smallest molecules are able to penetrate deeply into pores whereas the largest molecules are excluded by the smaller pore sizes. Figure 2.27 shows the regular instrumental setup of SEC.

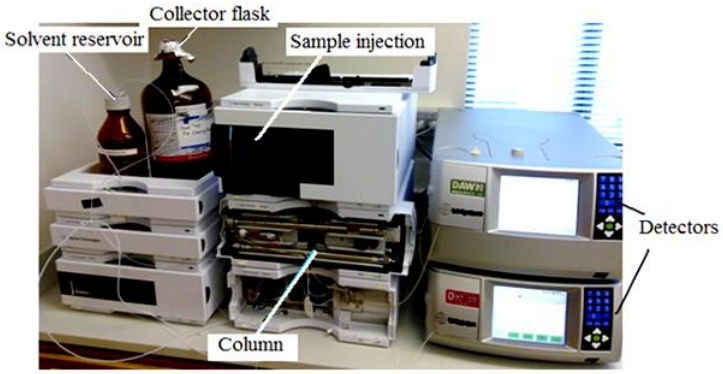


**Figure 2.27:** Regular instrumentation for size exclusion chromatography (SEC).

The properties of mobile phase are still important in that it is supposed to be strong affinity to stationary phase and be a good solubility to samples. The purpose of well soluble of sample is to make the polymer be perfect coil suspending in solution. Thus, as a mixture of solutes of different size passes through a column packed with porous particles. As shown in Figure 2.28, it clearly depicts the general idea for size separation by SEC. the main setup of SEC emphasizes three concepts: stationary phase (column), mobile phase (solvent) and sample preparation.

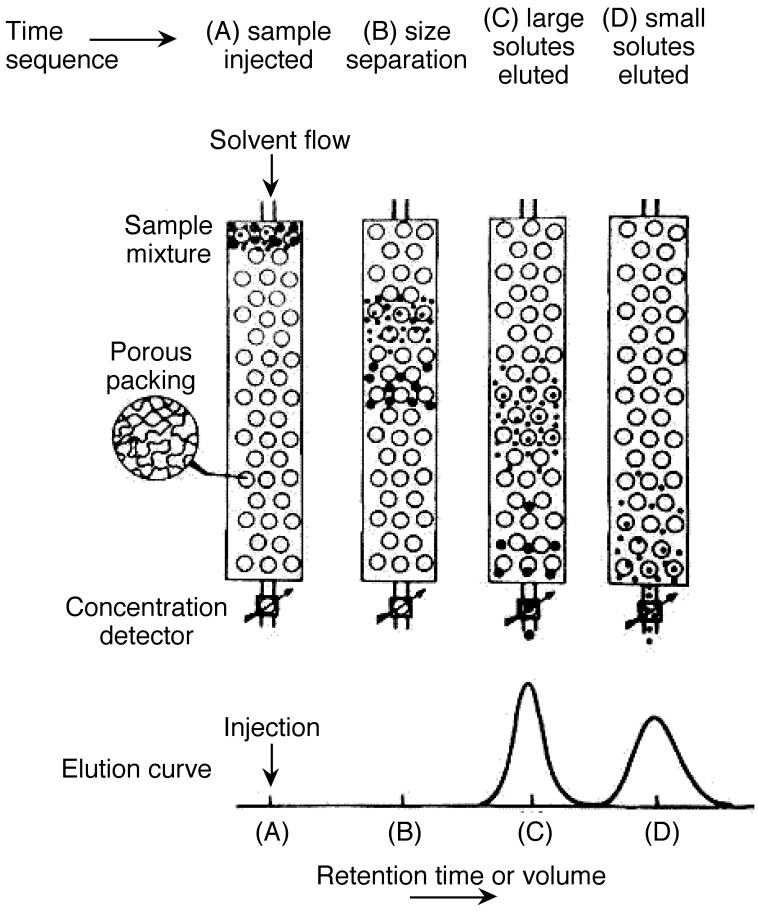


**Figure 2.28:** Development and detection of size separation by SEC. Adapted from A. M. Striegel, W. W. Yau, J. J. Kirkland, and D. D. Bly. *Modern Size-Exclusion Liquid Chromatography- Practice of Gel Permeation and Gel Filtration Chromatography,* 2nd Edition. Hoboken. N.J. (2009).

#### 2.2.3.3.1 Solvent selection

Solvent selection for SEC involves a number if considerations, such as convenience, sample type, column packing, operating variables, safety, and purity.

For samples concern, the solvents used for mobile phase of SEC are limited to those follows following criteria:

- The solvent must dissolve the sample completely.
- The solvent has different properties with solute in the eluent: typically with solvent refractive index (RI) different from the sample RI by $\pm$ 0.05 unit of more, or more than 10% of incident energy for UV detector.
- The solvent must not degrade the sample during use. Otherwise, the viscosity of eluent will gradually increase over times.
- The solvent is not corrosive to any components of the equipment.

Therefore, several solvents are qualified to be solvents such as THF, chlorinated hydrocarbons (chloroform, methylene chloride, dichloroethane, etc), aromatic hydrocarbons (benzene, toluene , trichlorobenzene, etc).

Normally, high purity of solvent (HPLC-grade) is recommended. The reasons are to avoid suspended particulates that may abrade the solvent pumping system or cause plugging of small-particle columns, to avoid impurities that may generate baseline noise, and to avoid impurities that are concentrated due to evaporation of solvent.

#### 2.2.3.3.2 Column selection

Column selection of SEC depends mainly on the desired molecular weight range of separation and the nature of the solvents and samples. Solute molecules should be separated solely by the size of gels without interaction of packing materials. Better column efficiencies and separations can be obtained with small particle packing in columns and high diffusion rates for sample solutes. Furthermore, optimal performance of an SEC packing materials involves high resolution and low column backpressure. Compatible solvent and column must be chosen because, for example, organic solvent is used to swell the organic column packing and used to dissolve and separate the samples.

It is convenient that columns are now usually available from manufacturers regarding the various types of samples. They provide the information such as maximum tolerant flow rates, backpressure tolerances, recommended sample concentration, and injection volumes, etc. Nonetheless, users have to notice a few things upon using columns:

- Vibration and extreme temperatures should be avoided because these will post irreversible damage on columns.
- For aqueous mobile phase, it is unwise to allow the extreme pH solutions staying in the columns for a long period of time.
- The columns should be stored with some neat organic mobile phase, or aqueous mobile phase with pH range 2 - 8 to prevent degradation of packing when not in use.

#### 2.2.3.3.3 Sample preparation

The sample solutions are supposed to be prepared in dilute concentration (less than 2 mg/mL) for several concerns. For polymer samples, samples must be dissolved in the solvent same as used for mobile phase except some special cases. A good solvent can dissolve a sample in any proportion in a range of temperatures. It is a slow process for dissolution because the rate determining step is solvent diffusion into polymers to produce swollen gels. Then, gradual disintegration of gels makes sample-solvent mixture truly become solution. Agitation and warming the mixtures are useful methods to speed up sample preparation.

It is recommended to filter the sample solutions before injecting into columns or storing in sample vials in order to get rid of clogging and excessively high pressure problems. If unfortunately the excessively high pressure or clogging occur due to higher concentration of sample solution, raising the column temperature will reduce the viscosity of the mobile phase, and may be helpful to redissolve the precipitated or adsorbed solutes in the column. Back flushing of the columns should only be used as the last resort.

### 2.2.3.4 Analysis of SEC data

The size exclusion separation mechanism is based on the effective hydrodynamic volume of the molecule, not the molecular weight, and therefore the system must be calibrated using standards of known molecular weight and homogeneous chemical composition. Then, the curve of sample is used to compare with calibration curve and obtain information relative to standards. The further step is required to covert relative molecular weight into absolute molecular weight of a polymer.

#### 2.2.3.4.1 Calibration

The purpose of calibration in SEC is to define the relationship between molecular weight and retention volume/time in the chosen permeation range of column set and to calculate the relative molecular weight to standard molecules. There are several calibration methods are commonly employed in modern SEC: direct standard calibration, poly-disperse standard calibration, universal calibration.

The most commonly used calibration method is direct standard calibration. In the direct standard calibration method, narrowly distributed standards of the same polymer being analyzed are used. Normally, narrow-molecular weight standards commercially available are polystyrene (PS). The molecular weight of standards are measured originally by membrane osmometry for number-average molecular weight, and by light scattering for weight-average molecular weight as described above. The retention volume at the peak maximum of each standard is equated with its stated molecular weight.

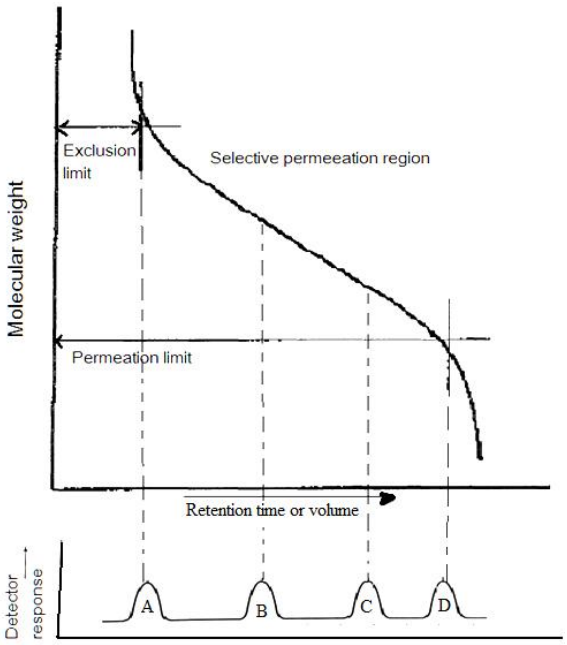


**Figure 2.29:** Calibration curve for a size-exclusion.

#### 2.2.3.4.2 Relative $M_w$ versus absolute $M_w$

The molecular weight and molecular weight distribution can be determined from the calibration curves as described above. But as the relationship between molecular weight and size depends on the type of polymer, the calibration curve depends on the polymer used, with the result that true molecular weight can only be obtained when the sample is the same type as calibration standards. As Figure 2.30 depicted, large deviations from the true molecular weight occur in the instance of branched samples because the molecular density of these is higher than in the linear chains.

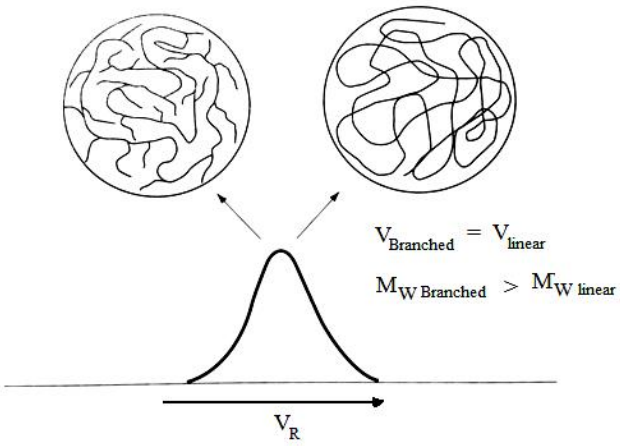


**Figure 2.30:** SEC elution of linear and branched samples of similar hydrodynamic volumes, but different molecular weights. S. Mori, and H. G. Barth. *Size Exclusion Chromatography*, Springer, New York. (1999).

Light-scattering detector is now often used to overcome the limitations of conventional SEC. These signals depend only on concentration, not on molecular weight or polymer size. For instance, for LS detector, (2.38) applies:

$$\text{LS signal} = K_{LS} \cdot (dn/dc)^2 \cdot M_w \cdot c \tag{2.38}$$

Where $K_{LS}$ is an apparatus-specific sensitivity constant, dn/dc is the refractive index increment and c is concentration. Therefore, accurate molecular weight can be determined while the concentration of the sample is known without calibration curve.

#### 2.2.3.5 A practical example

The syntheses of poly(3-hexylthiophene) are well developed during last decade. It is an attractive polymer due to its potential as electronic materials. Due to its excellent charge transport performances and high solubility, several studies discuss its further improvement such as making block copolymer even triblock copolymer. The details are not discussed here. However, the importance of molecular weight and molecular weight distribution is still critical.

As shown in Figure 2.31, they studied the mechanism of chain-growth polymerization and successfully produced low polydispersity P3HT. The figure also demonstrates that the molecule with larger molecular size/ or weight elutes out of the column earlier than those which has smaller molecular weight.

The real molecular weight of P3HT is smaller than the molecular weight relative to polystyrene. In this case, the backbone of P3HT is harder compared with polystyrenes' backbone because of the position of aromatic groups. It results in less flexibility. We can briefly judge the authentic molecular weight of the synthetic polymer according to its molecular structure.

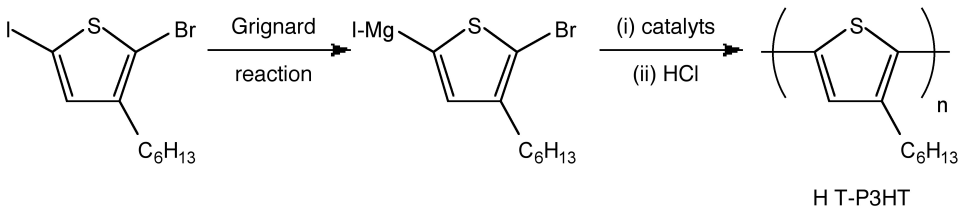


**Figure 2.31:** Synthesis of a well-defined poly(3-hexylthiphene) (HT-P3HT).

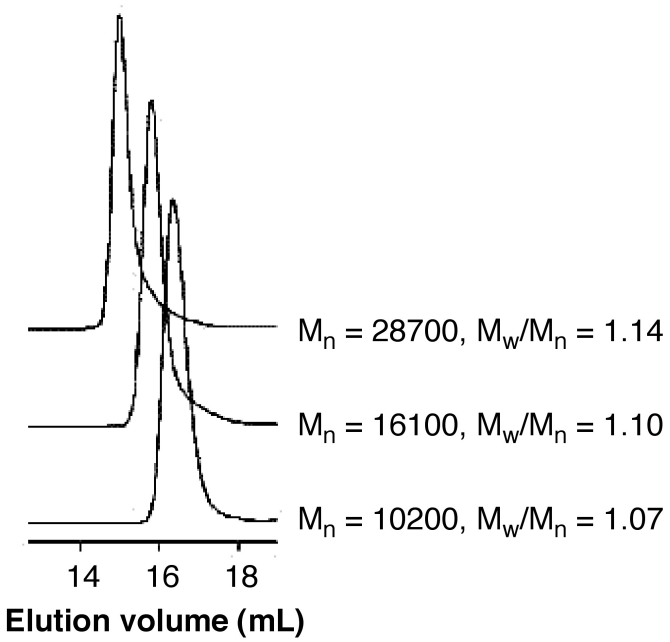


**Figure 2.32:** GPC profiles of HT-P3HT obtained by the polymerization. Adapted from R. Miyakoshi, A. Yokoyama, and T. Yokozawa, *Macromol. Rapid Commun.*, 2004, **25**, 1663.

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## 2.3 BET Surface Area Analysis of Nanoparticles[12]

### 2.3.1 Introduction

In the past few years, nanotechnology research has expanded out of the chemistry department and into the fields of medicine, energy, aerospace and even computing and information technology. With bulk materials, the surface area to volume is insignificant in relation to the number of atoms in the bulk, however when the particles are only 1 to 100 nm across, different properties begin to arise. For example, commercial grade zinc oxide has a surface area range of 2.5 to 12 $m^2/g$ while nanoparticle zinc oxide can have surface areas as high as 54 $m^2/g$ . The nanoparticles have superior UV blocking properties when compared to the bulk material, making them useful in applications such as sunscreen. Many useful properties of nanoparticles rise from their small size, making it very important to be able to determine their surface area.

### 2.3.2 Overview of BET theory

The BET theory was developed by Stephen Brunauer (Figure 2.33), Paul Emmett (Figure 2.34), and Edward Teller (Figure 2.35) in 1938. The first letter of each publisher's surname was taken to name this theory. The BET theory was an extension of the Langmuir theory, developed by Irving Langmuir (Figure 2.36) in 1916.

[12]This content is available online at <http://cnx.org/content/m38278/1.1/>.

**Figure 2.33:** Hungarian chemist Stephen Brunauer (1903-1986). Adapted from K. S. Sing, Langmuir, 1987, **3**, 2 (Copyright: American Chemical Society).

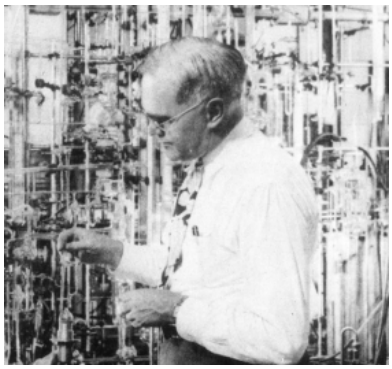

**Figure 2.34:** American chemical engineer Paul H. Emmett (1900 - 1985). Adapted from B.H. Davis, J. Phys. Chem., 1986, **90**, 4702 (Copyright: American Chemical Society).

**Figure 2.35:** Hungarian born theoretical physicist Edward Teller (1908 – 2003) shown in 1958 as the director of Lawrence Livermore National Laboratory was known as "the father of the hydrogen bomb".

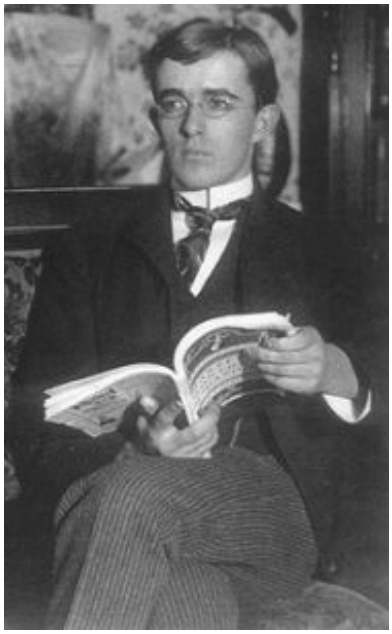

**Figure 2.36:** American chemist and physicist Irving Langmuir (1881 - 1957). Adapted from *J. Chem. Educ.*, 1933, **10**, 65 (Copyright: American Chemical Society).

The Langmuir theory relates the monolayer adsorption of gas molecules (Figure 2.37), also called adsorbates, onto a solid surface to the gas pressure of a medium above the solid surface at a fixed temperature to

(2.39), where $\theta$ is the fractional cover of the surface, P is the gas pressure and $\alpha$ is a constant.

$$\theta = \frac{\alpha \cdot P}{1 + (\alpha \cdot P)} \tag{2.39}$$

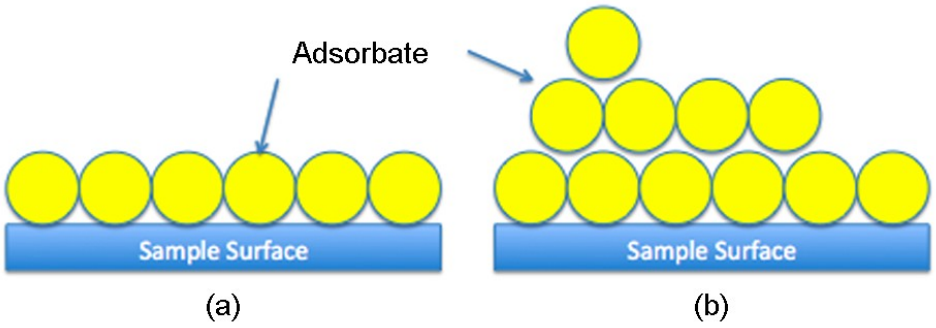


**Figure 2.37:** Schematic of the adsorption of gas molecules onto the surface of a sample showing (a) the monolayer adsorption model assumed by the Langmuir theory and (b) s the multilayer adsorption model assumed by the BET theory.

The Langmuir theory is based on the following assumptions:

- All surface sites have the same adsorption energy for the adsorbate, which is usually argon, krypton or nitrogen gas. The surface site is defined as the area on the sample where one molecule can adsorb onto.
- Adsorption of the solvent at one site occurs independently of adsorption at neighboring sites.
- Activity of adsorbate is directly proportional to its concentration.
- Adsorbates form a monolayer.
- Each active site can be occupied only by one particle.

The Langmuir theory has a few flaws that are addressed by the BET theory. The BET theory extends the Langmuir theory to multilayer adsorption (Figure 2.37) with three additional assumptions:

- Gas molecules will physically adsorb on a solid in layers infinitely.
- The different adsorption layers do not interact.
- The theory can be applied to each layer.

### 2.3.3 How does BET work?

Adsorption is defined as the adhesion of atoms or molecules of gas to a surface. It should be noted that adsorption is not confused with absorption, in which a fluid permeates a liquid or solid. The amount of gas adsorbed depends on the exposed surface are but also on the temperature, gas pressure and strength of interaction between the gas and solid. In BET surface area analysis, nitrogen is usually used because of its availability in high purity and its strong interaction with most solids. Because the interaction between gaseous and solid phases is usually weak, the surface is cooled using liquid $N_2$ to obtain detectable amounts

of adsorption. Known amounts of nitrogen gas are then released stepwise into the sample cell. Relative pressures less than atmospheric pressure is achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure. Highly precise and accurate pressure transducers monitor the pressure changes due to the adsorption process. After the adsorption layers are formed, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified. The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure. There are five types of adsorption isotherms possible.

#### 2.3.3.1 Type I isotherm

Type I is a pseudo-Langmuir isotherm because it depicts monolayer adsorption (Figure 2.38). A type I isotherm is obtained when $P/P_o < 1$ and $c > 1$ in the BET equation, where $P/P_o$ is the partial pressure value and c is the BET constant, which is related to the adsorption energy of the first monolayer and varies from solid to solid. The characterization of microporous materials, those with pore diameters less than 2 nm, gives this type of isotherm.

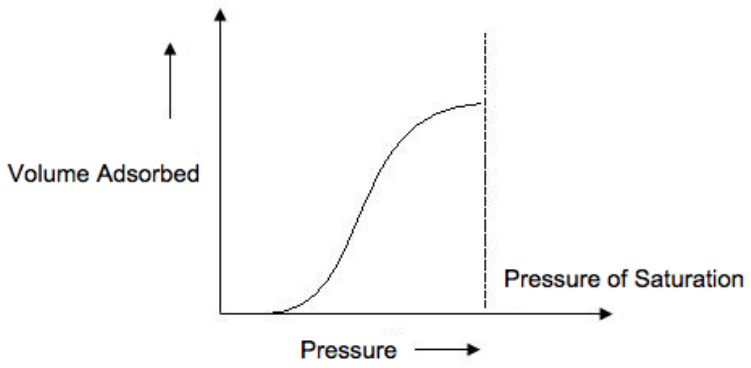


**Figure 2.38:** The isotherm plots the volume of gas adsorbed onto the surface of the sample as pressure increases. Adapted from S. Brunauer L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

#### 2.3.3.2 Type II isotherm

A type II isotherm (Figure 2.39) is very different than the Langmuir model. The flatter region in the middle represents the formation of a monolayer. A type II isotherm is obtained when $c > 1$ in the BET equation. This is the most common isotherm obtained when using the BET technique. At very low pressures, the micropores fill with nitrogen gas. At the knee, monolayer formation is beginning and multilayer formation occurs at medium pressure. At the higher pressures, capillary condensation occurs.

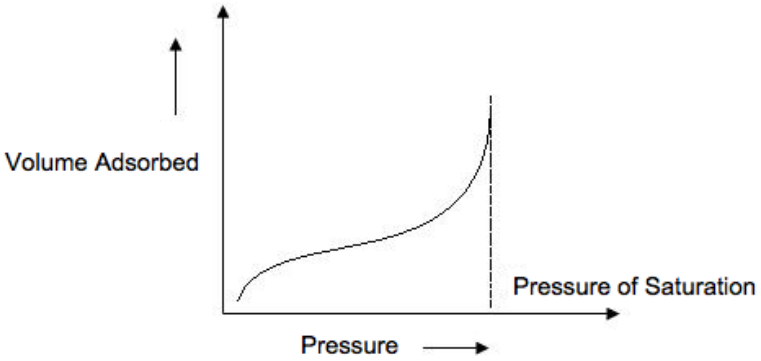


**Figure 2.39:** The isotherm plots the volume of gas adsorbed onto the surface of the sample as pressure increases. Adapted from S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

#### 2.3.3.3 Type III isotherm

A type III isotherm (Figure 2.40) is obtained when the c $<$ 1 and shows the formation of a multilayer. Because there is no asymptote in the curve, no monolayer is formed and BET is not applicable.

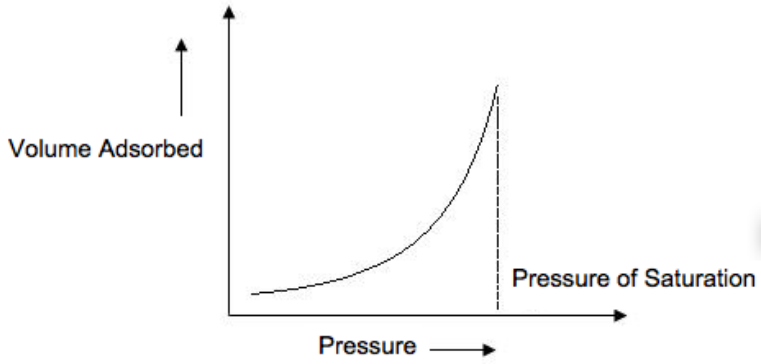


**Figure 2.40:** Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, *62*, 1723.

### 2.3.3.4 Type IV isotherm

Type IV isotherms (Figure 2.41) occur when capillary condensation occurs. Gases condense in the tiny capillary pores of the solid at pressures below the saturation pressure of the gas. At the lower pressure regions, it shows the formation of a monolayer followed by a formation of multilayers. BET surface area characterization of mesoporous materials, which are materials with pore diameters between 2 - 50 nm, gives this type of isotherm.

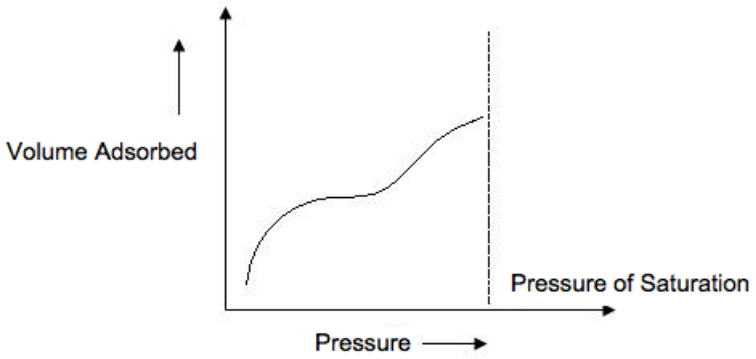


**Figure 2.41:** Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, *62*, 1723.

### 2.3.3.5 Type V isotherm

Type V isotherms (Figure 2.42) are very similar to type IV isotherms and are not applicable to BET.

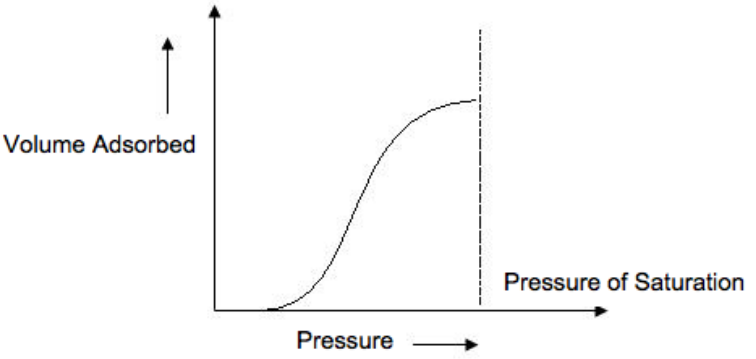


**Figure 2.42:** Brunauer L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

## 2.3.4 Calculations

The BET equation, (2.40), uses the information from the isotherm to determine the surface area of the sample, where X is the weight of nitrogen adsorbed at a given relative pressure (P/Po), $X_m$ is monolayer capacity, which is the volume of gas adsorbed at standard temperature and pressure (STP), and C is constant. STP is defined as 273 K and 1 atm.

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C}\left(\frac{P}{P_0}\right) \tag{2.40}$$

### 2.3.4.1 Multi-point BET

Ideally five data points, with a minimum of three data points, in the $P/P_0$ range 0.025 to 0.30 should be used to successfully determine the surface area using the BET equation. At relative pressures higher than 0.5, there is the onset of capillary condensation, and at relative pressures that are too low, only monolayer formation is occurring. When the BET equation is plotted, the graph should be of linear with a positive slope. If such a graph is not obtained, then the BET method was insufficient in obtaining the surface area.

- The slope and y-intercept can be obtained using least squares regression.
- The monolayer capacity $X_m$ can be calculated with (2.41).
- Once $X_m$ is determined, the total surface area $S_t$ can be calculated with the following equation, where $L_{av}$ is Avogadro's number, $A_m$ is the cross sectional area of the adsorbate and equals 0.162 $nm^2$ for an absorbed nitrogen molecule, and $M_v$ is the molar volume and equals 22414 mL, (2.42).

$$X_m = \frac{1}{s+i} = \frac{C-1}{Cs} \tag{2.41}$$

$$S = \frac{X_m L_{av} A_m}{M_v} \tag{2.42}$$

Single point BET can also be used by setting the intercept to 0 and ignoring the value of C. The data point at the relative pressure of 0.3 will match up the best with a multipoint BET. Single point BET can be used over the more accurate multipoint BET to determine the appropriate relative pressure range for multi-point BET.

## 2.3.5 Sample preparation and experimental setup

Prior to any measurement the sample must be degassed to remove water and other contaminants before the surface area can be accurately measured. Samples are degassed in a vacuum at high temperatures. The highest temperature possible that will not damage the sample's structure is usually chosen in order to shorten the degassing time. IUPAC recommends that samples be degassed for at least 16 hours to ensure that unwanted vapors and gases are removed from the surface of the sample. Generally, samples that can withstand higher temperatures without structural changes have smaller degassing times. A minimum of 0.5 g of sample is required for the BET to successfully determine the surface area.

Samples are placed in glass cells to be degassed and analyzed by the BET machine. Glass rods are placed within the cell to minimize the dead space in the cell. Sample cells typically come in sizes of 6, 9 and 12 mm and come in different shapes. 6 mm cells are usually used for fine powders, 9 mm cells for larger particles and small pellets and 12 mm are used for large pieces that cannot be further reduced. The cells are placed into heating mantles and connected to the outgas port of the machine.

After the sample is degassed, the cell is moved to the analysis port (Figure 2.43). Dewars of liquid nitrogen are used to cool the sample and maintain it at a constant temperature. A low temperature must be

maintained so that the interaction between the gas molecules and the surface of the sample will be strong enough for measurable amounts of adsorption to occur. The adsorbate, nitrogen gas in this case, is injected into the sample cell with a calibrated piston. The dead volume in the sample cell must be calibrated before and after each measurement. To do that, helium gas is used for a blank run, because helium does not adsorb onto the sample.

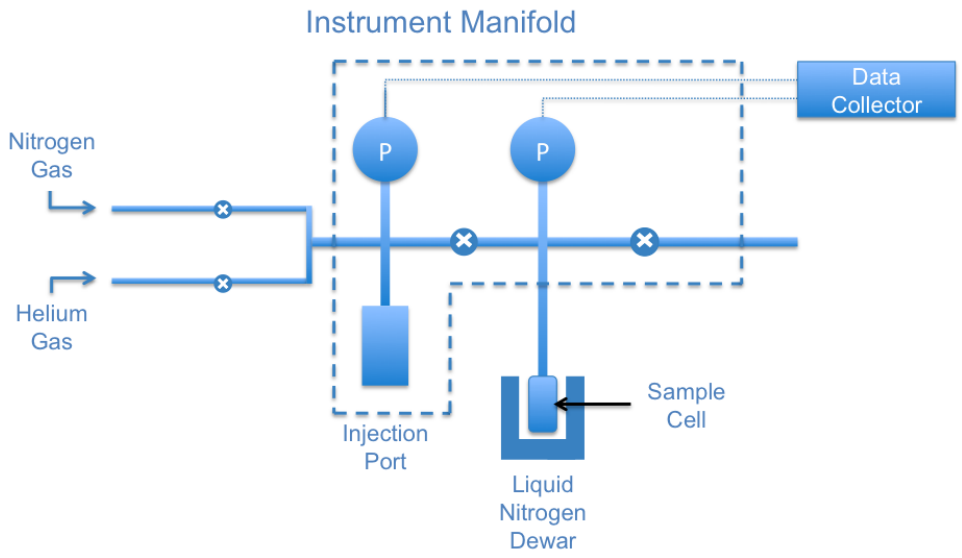


**Figure 2.43:** Schematic representation of the BET instrument. The degasser is not shown.

### 2.3.6 Shortcomings of BET

The BET technique has some disadvantages when compared to NMR, which can also be used to measure the surface area of nanoparticles. BET measurements can only be used to determine the surface area of dry powders. This technique requires a lot of time for the adsorption of gas molecules to occur. A lot of manual preparation is required.

### 2.3.7 The surface area determination of metal-organic frameworks

The BET technique was used to determine the surface areas of metal-organic frameworks (MOFs), which are crystalline compounds of metal ions coordinated to organic molecules. Possible applications of MOFs, which are porous, include gas purification and catalysis. An isoreticular MOF (IRMOF) with the chemical formula $Zn_4O$(pyrene-1,2-dicarboxylate)$_3$ (Figure 2.44) was used as an example to see if BET could accurately determine the surface area of microporous materials. The predicted surface area was calculated directly from the geometry of the crystals and agreed with the data obtained from the BET isotherms. Data was collected at a constant temperature of 77 K and a type II isotherm (Figure 2.45) was obtained.

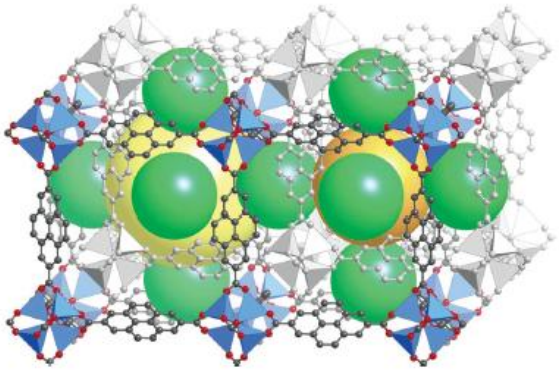

**Figure 2.44:** The structure of catenated IRMOF-13. Orange and yellow represent non-catenated pore volumes. Green represents catenated pore volume.

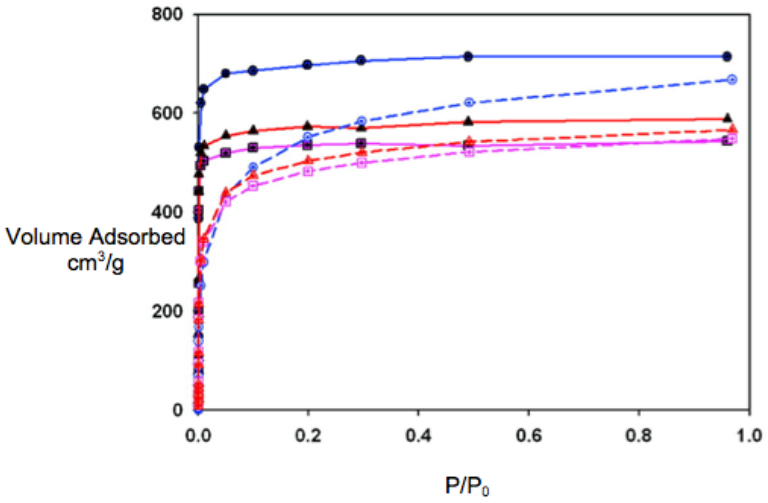


**Figure 2.45:** The BET isotherms of the zeolites and metal-organic frameworks. IRMOF-13 is symbolized by the black triangle and red line. Adapted from Y.S. Bae, R.Q. Snurr, and O. Yazaydin, *Langmuir*, 2010, **26**, 5478.

The isotherm data obtained from partial pressure range of 0.05 to 0.3 is plugged into the BET equation, (2.40), to obtain the BET plot (Figure 2.46).

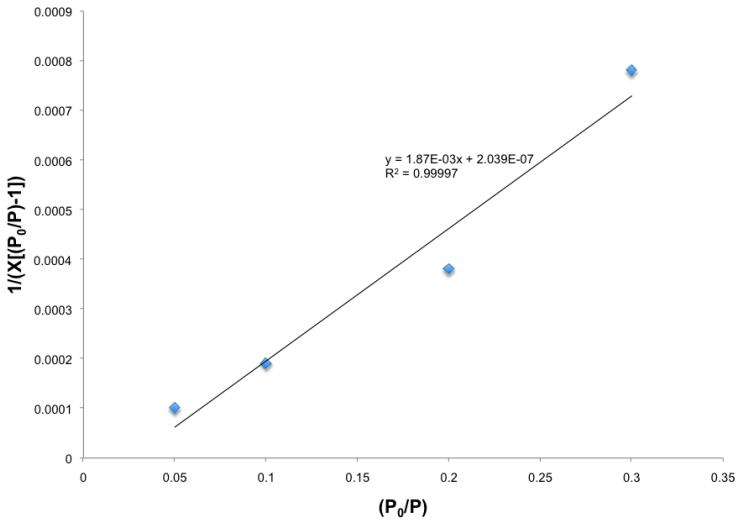


**Figure 2.46:** BET plot of IRMOF-13 using points collected at the pressure range 0.05 to 0.3. The equation of the best-fit line and $R^2$ value are shown. Adapted from Y.S. Bae, R.Q. Snurr, and O. Yazaydin, *Langmuir*, 2010, **26**, 5479.

Using (2.43), the monolayer capacity is determined to be 391.2 $cm^3/g$.

$$X_m = \frac{1}{(2.66E-3)+(-5.512E-05)} \tag{2.43}$$

Now that $X_m$ is known, then (2.44) can be used to determine that the surface area is 1702.3 $m^2/g$.

$$S = \frac{391.2cm^3 * 0.162nm^2 * 6.02 * 10^{23}}{22.414L} \tag{2.44}$$

## 2.3.8 Bibliography


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