Polymer Size and Shape

- The general problem of the size and shape of polymer molecules is the heart of polymer science and engineering.

- If the molecular weight and molecular weight distribution (MWD) are known along with a good understanding of the polymer chain conformation, many mechanical and rheological properties can be predicted.

- Polymers have presented several special problems:
  - 1- The molecular weights of polymers are very high, ranging from about 25,000 to 1,000,000 g/mol or higher.
Polymer Size and Shape

• At lower molecular weights, the term oligomer is used for a polymer with only a few repeat units, having degrees of polymerization of not more than 10 to 100. Assuming a molecular weight of 50 g/mol for each mer, a range of molecular weights of up to 500 to 5000 g/mol result.

• The molecular weight of ordinary size molecules is fixed (e.g., benzene has a molecular weight of 78 g/mol regardless of its source).

• Most polymer molecular weights vary greatly depending on the method of preparation.

• Most polymers are polydisperse; that is, the sample contains more than one species.

Polymer Size and Shape

• 3. The spatial arrangement of the polymer chain is called its “conformation.”

• Conformations can be determined in dilute solutions by light scattering, and in the bulk state by small-angle neutron scattering (SANS).

• Conformations can also be estimated theoretically from the structure and molecular weight of the polymer.

• Polymer chain conformations are functions of temperature, solvent, structure, crystallization, extension, and the presence of other polymers.
Polymer Size and Shape

- 4. Another major problem in the polymer industry is that of rapid molecular weight determination.

- The initial supplier synthesizes different lots of the same or perhaps slightly different polymeric materials every day.

- The manufacturer needs to know not only the molecular weight, but also the molecular weight distribution of each lot to optimize the settings on the factory’s processing equipment.

Polymer Solutions

- Most of the methods for determining the molecular weight and size of polymers (except for small-angle neutron scattering) depend on dissolving the polymer in an appropriate solvent and measuring the required properties in dilute solution.

- The molecular weights of gaseous molecules such as oxygen or methane can be determined via an understanding of the gas laws and the fact that the molecules are separated in space. The same is true for polymer solutions.

- So we should know the basic polymer solution thermodynamics for the purposes of determining molecular weights and sizes.
Polymer Solutions

- One of the simplest notions in chemistry is that “like dissolves like.”
  Qualitatively, “like” may be defined variously in terms of similar chemical groups or similar polarities.
- Quantitatively, solubility of one component in another is governed by the familiar equation of the free energy of mixing

\[
\Delta G_M = \Delta H_M - T \Delta S_M
\]

- where \( \Delta G_M \) is the change in Gibbs’ free energy on mixing, \( T \) is the absolute temperature, and \( \Delta S_M \) is the entropy of mixing.
- A negative value of \( \Delta G_M \) indicates that the solution process will occur spontaneously.

Polymer Solutions

- The term \( T\Delta S_M \) is always positive because there is an increase in the entropy on mixing. (note the negative sign)

- Therefore the sign of \( \Delta G_M \) depends on the magnitude of \( \Delta H_M \), the enthalpy of mixing.

\[
\Delta G_M = \Delta H_M - T \Delta S_M
\]

- The heat of mixing is usually positive, opposing mixing. This is true for big and little molecules alike.
Polymer Solutions

- Exceptions occur most frequently when the two species in question attract one another in some way, perhaps by having opposite polarities, being acid and base relative to one another, or through hydrogen bonding.

- However, positive heats of mixing are the more usual case for relatively nonpolar organic compounds.

\[ \Delta G_M = \Delta H_M - T \Delta S_M \]

Polymer Solutions

- On a quantitative basis, Hildebrand and Scott proposed that, for regular solutions:

\[ \Delta H_M = V_M \left( \frac{\Delta E_1}{V_1} \right)^{1/2} - \left( \frac{\Delta E_2}{V_2} \right)^{1/2} \] \[ v_1 v_2 \]

- \( V_M \) represents the total volume of the mixture.
- \( \Delta E \) represents the energy of vaporization to a gas at zero pressure (i.e., at infinite separation of the molecules).
- \( V \) is the molar volume of the components, for both species 1 and 2.
- \( v \) represents the volume fraction of component 1 or 2 in the mixture.
- The quantity \( \Delta E/V \) represents the energy of vaporization per unit volume. This term is sometimes called the cohesive energy density.
THE SOLUBILITY PARAMETER

According to Hildebrand equation, “like dissolves like” means that the two terms \( \Delta E_1/V_1 \) and \( \Delta E_2/V_2 \) have nearly the same numerical values.

It also yields only positive values of \( \Delta H_M \), a serious fault in the theory.

However, since the majority of polymer solutions do have positive heats of mixing, the theory has found very considerable application.

The square root of the cohesive energy density is widely known as the solubility parameter

\[
\delta = \left( \frac{\Delta E}{V} \right)^{1/2}
\]

THE SOLUBILITY PARAMETER

The heat of mixing of two substances is dependent on \( (\delta_1 - \delta_2)^2 \).

These relationships are meaningful only for positive heats of mixing; that is, when the heat of mixing term opposes solution.

Since \( (\delta_1 - \delta_2)^2 \) cannot be negative, these equations break down for negative heats of mixing.

Solubility tables provide a quantitative basis for understanding why methanol or water does not dissolve polybutadiene or polystyrene.

However, benzene and toluene are predicted to be good solvents for these polymers, which they are.
THE SOLUBILITY PARAMETER

- While solubility of a polymer also depends on its molecular weight, the temperature, and so on, it is frequently found that polymers will dissolve in solvents having solubility parameters within about one unit of their own, in (cal/cm$^3$)$^{1/2}$.

- Hydrogen bonding is an important secondary parameter in predicting solubility.

---

THE SOLUBILITY PARAMETER (solvents)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>$\mu$ (MPa$^{1/2}$)</th>
<th>H-bonding$^a$ Group</th>
<th>Specific Gravity$^a$ 20°C (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>9.9</td>
<td>20.3</td>
<td>m</td>
<td>0.7899</td>
</tr>
<tr>
<td>Benzene</td>
<td>9.2</td>
<td>18.8</td>
<td>p</td>
<td>0.87865</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>8.5</td>
<td>17.4</td>
<td>m</td>
<td>0.8885</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.6</td>
<td>17.6</td>
<td>p</td>
<td>1.5940</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>8.2</td>
<td>16.8</td>
<td>p</td>
<td>0.7785</td>
</tr>
<tr>
<td>n-Decane</td>
<td>6.6</td>
<td>13.5</td>
<td>p</td>
<td>—</td>
</tr>
<tr>
<td>Dibutyl amine</td>
<td>8.1</td>
<td>16.6</td>
<td>s</td>
<td>—</td>
</tr>
<tr>
<td>Dichlorodichloromethane</td>
<td>5.5</td>
<td>11.3</td>
<td>p</td>
<td>—</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>7.9</td>
<td>16.2</td>
<td>m</td>
<td>1.0337</td>
</tr>
<tr>
<td>Low odor mineral spirits</td>
<td>6.9</td>
<td>14.1</td>
<td>p</td>
<td>—</td>
</tr>
<tr>
<td>Methanol</td>
<td>14.5</td>
<td>29.7</td>
<td>s</td>
<td>0.7914</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.9</td>
<td>18.2</td>
<td>p</td>
<td>0.8669</td>
</tr>
<tr>
<td>Turpentine</td>
<td>8.1</td>
<td>16.6</td>
<td>p</td>
<td>—</td>
</tr>
<tr>
<td>Water</td>
<td>23.4</td>
<td>47.9</td>
<td>s</td>
<td>0.99823</td>
</tr>
<tr>
<td>Xylene</td>
<td>8.8</td>
<td>18.0</td>
<td>p</td>
<td>0.8611</td>
</tr>
</tbody>
</table>


- p, Poorly H-bonded; m, moderately H-bonded; and s, strongly H-bonded.
Experimental Determination of solubility parameter

- The solubility parameter of a new polymer may be determined by any of several means.

- If the polymer is cross-linked, the solubility parameter may be determined by swelling experiments.

- The best solvent is defined for the purposes of the experiment as the one with the closest solubility parameter. This solvent also swells the polymer the most.

- Several solvents of varying solubility parameters are selected, and the cross-linked polymer is swelled to equilibrium in each of them.

---

**Table 3.2 Solubility parameters and densities of common polymers (6)**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>$\delta$ (MPa)$^{1/2}$</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene</td>
<td>8.4</td>
<td>17.2</td>
<td>1.01</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>7.9</td>
<td>16.2</td>
<td>0.85 (amorphous)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>9.45</td>
<td>19.4</td>
<td>1.188</td>
</tr>
<tr>
<td>Polytetrafluorethylene</td>
<td>6.2</td>
<td>12.7</td>
<td>2.00 amorphous, estimated</td>
</tr>
<tr>
<td>Polyisobutene</td>
<td>7.85</td>
<td>16.5</td>
<td>0.917</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>9.10</td>
<td>18.6</td>
<td>1.06</td>
</tr>
<tr>
<td>Cellulose triacetate (50% ac groups)</td>
<td>13.60</td>
<td>27.8</td>
<td>1.28*</td>
</tr>
<tr>
<td>Cellulose tributyrate</td>
<td>—</td>
<td>—</td>
<td>1.16'</td>
</tr>
<tr>
<td>Polyamide 66</td>
<td>13.6</td>
<td>22.9</td>
<td>1.24</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>9.9</td>
<td>20.0</td>
<td>1.20</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate), partly crystalline</td>
<td>10.7</td>
<td>21.9</td>
<td>1.38</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate), amorphous</td>
<td>10.7</td>
<td>21.9</td>
<td>1.34</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>12.6</td>
<td>25.8</td>
<td>1.26</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>9.6</td>
<td>19.8</td>
<td>1.39</td>
</tr>
</tbody>
</table>

*Note: $1 \text{ (cal/cm}^3)^{1/2} = 2.046 \times 10^3 \text{ (J/m}^3)^{1/2}.$*
Experimental Determination of solubility parameter

• The swelling coefficient, \( Q \), is plotted against the various solvent’s solubility parameter, the maximum defining the solubility parameter of the polymer.

\[
Q = \frac{m - m_0}{m_0} \times \frac{1}{\rho_s}
\]

• where \( m \) is the weight of the swollen sample, \( m_0 \) is the dry weight, and \( \rho_s \) is the density of the swelling agent.

Polyurethane (■), polystyrene (▲), and a polyurethane–polystyrene interpenetrating polymer networks (●).

Experimental Determination of solubility parameter

• the solubility parameter may be determined by measuring the intrinsic viscosity of the polymer in these solvents, if the polymer is soluble in them.

• Then the intrinsic viscosity is plotted against the solubility parameter of the several solvents.

• Since the chain conformation is most expanded in the best solvent the intrinsic viscosity will be highest for the best match in solubility parameter.

polyisobutene (A) and polystyrene (B)
Theoretical Calculation of solubility parameter

- Values of the solubility parameter may be calculated from a knowledge of the chemical structure of any compound, polymer or otherwise. Use is made of the group molar attraction constants, $G$, for each group

$$\delta = \frac{\rho \sum G}{M}$$

- Where $\rho$ represents the density and $M$ is the molecular weight. For a polymer, $M$ is the mer molecular weight.

---

Theoretical Calculation of solubility parameter

Group molar attraction constants at 25°C according to Small and Hoy

<table>
<thead>
<tr>
<th>Group</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\text{CH}_3$</td>
<td>214</td>
</tr>
<tr>
<td>$-\text{CH}_2$</td>
<td>190</td>
</tr>
<tr>
<td>$-\text{CH}$</td>
<td>133</td>
</tr>
<tr>
<td>$&gt;-\text{C}&lt;-$</td>
<td>$-93$</td>
</tr>
<tr>
<td>$\equiv \equiv$</td>
<td>10</td>
</tr>
<tr>
<td>$&gt;\equiv \equiv$</td>
<td>111</td>
</tr>
<tr>
<td>$-\equiv &gt;$</td>
<td>285</td>
</tr>
<tr>
<td>$-\equiv \equiv$</td>
<td>222</td>
</tr>
<tr>
<td>Phenyl</td>
<td>735</td>
</tr>
<tr>
<td>Phenylene (o, m, p)</td>
<td>658</td>
</tr>
<tr>
<td>Naphthyl</td>
<td>1146</td>
</tr>
</tbody>
</table>

Units of $G = (\text{cal-cm}^3)^{1/2}/\text{mol}$

<table>
<thead>
<tr>
<th>Group</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring 5-membered</td>
<td>105-115</td>
</tr>
<tr>
<td>Ring 6-membered</td>
<td>95-105</td>
</tr>
<tr>
<td>Conjugation</td>
<td>20-30</td>
</tr>
<tr>
<td>H (variable)</td>
<td>80-100</td>
</tr>
<tr>
<td>O ethers</td>
<td>70</td>
</tr>
<tr>
<td>CO ketones</td>
<td>275</td>
</tr>
<tr>
<td>COO esters</td>
<td>310</td>
</tr>
<tr>
<td>CN</td>
<td>410</td>
</tr>
<tr>
<td>Cl (mean)</td>
<td>260</td>
</tr>
<tr>
<td>Cl single</td>
<td>270</td>
</tr>
<tr>
<td>Cl twinned as in $&gt;\text{CCl}_2$</td>
<td>260</td>
</tr>
<tr>
<td>Cl triple as in $&gt;-\text{CCl}_2$</td>
<td>250</td>
</tr>
</tbody>
</table>
Theoretical Calculation of solubility parameter (Example)

- Calculate the solubility parameter of polystyrene by the group contribution method. The density of polystyrene is 1.05 g/cm³, and the mer molecular weight is 104 g/mol

\[ \delta = 9.05 \text{(cal/cm}^3\text{)}^{1/2} \]

Surface tension & Interfacial tension

- The molecules at the surface are missing half their attractive interactions
- Unbalanced forces for the molecules at the surface lead to additional energy
- The additional free energy at the surface is known as surface energy

- \( \gamma = \) specific free energy or surface tension
- Specific surface energy of a material is the excess energy per unit area due to the existence of the free surface
Surface tension & Interfacial tension

- Surface energy is a direct manifestation of intermolecular forces.

**Surface tension of a few common liquids in mJ/m²**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Helium (4 K)</th>
<th>Ethanol</th>
<th>Acetone</th>
<th>Glycerol</th>
<th>Water (100°C)</th>
<th>Molten glass</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>23</td>
<td>24</td>
<td>63</td>
<td>73</td>
<td>-300</td>
<td>485</td>
</tr>
</tbody>
</table>

- The additional free energy at the interface between two condensed phases is known as interfacial energy:

\[ \gamma_{12} = \gamma_1 + \gamma_2 - W_{12} \]

THERMODYNAMICS OF MIXING

- *Statistical Thermodynamics of Mixing*
  - According to statistical thermodynamics, the entropy of mixing is determined by counting the number of possible arrangements in space that the molecules may assume, \( \Omega \).

- The change in entropy of mixing is given by Boltzmann’s relation

\[ \Delta S_M = k \ln \Omega \]

- For small molecules of about the same size, this is given by the total number of ways of arranging the \( N_2 \) identical molecules of the solute on a lattice comprising \( N_0 = N_1 + N_2 \) cells

- The total number of such arrangements:

\[ \Omega = \frac{N_0!}{N_1!N_2!} \]
Statistical Thermodynamics of Mixing

- Applying Stirling’s approximation

\[ \ln N! = N \ln N - N \]

- the entropy of mixing is given by

\[ \Delta S_M = k[(N_1 + N_2) \ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2] \]

\[ \Rightarrow \Delta S_M = -k(N_1 \ln \nu_1 + N_2 \ln \nu_2) \]
Statistical Thermodynamics of Mixing

- When the polymer has \( x \) chain segments (mers), the entropy of mixing is given by

\[
\Delta S_M = -k(N_1 \ln v_1 + N_2 \ln v_2)
\]

\[
v_1 = \frac{N_1}{N_1 + xN_2}
\]

\[
v_2 = \frac{xN_2}{N_1 + xN_2}
\]

- \( v_1 \) and \( v_2 \) represent the volume fractions of solvent and polymer, respectively.

Statistical Thermodynamics of Mixing

- For polymer–polymer solutions

\[
v_1 = \frac{x_1N_1}{x_1N_1 + x_2N_2}
\]

\[
v_2 = \frac{x_2N_2}{x_1N_1 + x_2N_2}
\]

- \( \Delta S_M \) is the combinatorial entropy computed by considering the possible arrangements of the molecules on the lattice.

- The number of ways that the system can be rearranged in space is reduced when one or both of the species exist as long chains.

- In the equations above, the subscript 1 usually represents the solvent, and the subscript 2 the polymer.
Different types of solutions

- An ideal solution is characterized by an enthalpy of mixing equal to zero and an entropy of mixing equal to the conformational entropy (or combinatorial entropy);
- An athermal solution is also characterized by an enthalpy of mixing equal to zero but its entropy of mixing is higher than the conformational entropy. It thus exhibits an excess entropy;
- A regular solution is characterized by a nonzero enthalpy of mixing and an entropy of mixing equal to the conformational entropy;
- An irregular (or real) solution corresponds to a solution whose enthalpy of mixing does not equal zero and whose entropy of mixing comprises an excess entropy in addition to the conformational term;

Dilute Solutions

- The Flory–Huggins theory introduces the unitless quantity $\chi$ to represent the heat of mixing

$$\Delta H_{\text{mix}} = k T \chi_{12} N_1 N_2$$

- where $\chi_{12}$ is called polymer–solvent interaction parameter. Which leads to the free energy of mixing in statistical thermodynamic terms

$$\Delta G_M = k T (N_1 \ln v_1 + N_2 \ln v_2 + \chi_{12} N_1 N_2)$$

- The first two terms of $\Delta G$ equation are entropic, while the last term on the right is enthalpic. Incompressibility is assumed, meaning that the free volume in the system is constant.
Dilute Solutions

\[ \Delta G_M = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \]

- \( \Delta G \) equation provides a starting point for many equations of interest. The partial molar free energy of mixing may be written, after multiplying by Avogadro’s number

\[ \overline{\Delta G_1} = RT \left[ \ln(1 - v_2) + \left(1 - \frac{1}{x}\right)v_2 + \chi_1 v_2^2 \right] \]

- Since the osmotic pressure is given by

\[ \pi = -\frac{\overline{\Delta G_1}}{V_1} \]

- where \( V_1 \) represents the molar volume of the solvent.

Dilute Solutions

\[ \pi = -\frac{RT}{V_1} \left[ \ln(1 - v_2) + \left(1 - \frac{1}{x}\right)v_2 + \chi_1 v_2^2 \right] \]

- On expanding the above equation, the theoretical value for the second virial coefficient can be separated out.

\[ A_2 = \frac{\rho_1}{M_1 \rho_2^2} \left( \frac{1}{2} - \chi_1 \right) \]

- \( \rho_1, \rho_2 \) and \( M_1 \) are solvent density, polymer density and solvent molecular weight respectively.
Values for the Flory–Huggins $\chi_1$ Parameter

- The Flory–Huggins $\chi_1$ parameter has been one of the most widely used quantities.  
  \[ \chi_{12} \equiv \frac{V_m (\delta_1 - \delta_2)^2}{RT} \quad X_1 = \beta_1 + \frac{V_i}{RT} (\delta_1 - \delta_2)^2 \]

- It is a unitless number. Sometimes the Flory–Huggins parameter is written $\chi_{1,2}$, and sometimes just plain $\chi$.

- While the original theory proposed that $\chi_1$ be concentration independent, many polymer–solvent systems exhibit increases of $\chi_1$ with polymer concentration which can be written as a power series,
  
  \[ \chi_1 = A + B \phi_2 + C \phi_2^2 \]

Values for the Flory–Huggins $\chi_1$ Parameter

- for many simple calculations, it is valuable to have a single number parameter.
- Typical values of $\chi_1$ are illustrated in Table 3.4, where values were selected at low concentrations of polymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>$T$, °C</th>
<th>$\chi_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Toluene</td>
<td>25</td>
<td>0.37</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Cyclohexane</td>
<td>34</td>
<td>0.50</td>
</tr>
<tr>
<td>Polysoprene</td>
<td>Benzene</td>
<td>25</td>
<td>0.40</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>Acetone</td>
<td>20</td>
<td>0.14</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>$n$-Propylacetate</td>
<td>20</td>
<td>-0.38</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>Benzene</td>
<td>70</td>
<td>0.19</td>
</tr>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>Toluene</td>
<td>20</td>
<td>0.45</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>$n$-Heptane</td>
<td>109</td>
<td>0.29</td>
</tr>
<tr>
<td>Poly(butadiene–styrene)</td>
<td>Toluene</td>
<td>25</td>
<td>0.39</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>Water</td>
<td>25</td>
<td>0.4³</td>
</tr>
</tbody>
</table>
Values for the Flory–Huggins $\chi_1$ Parameter

- If the value of $\chi_1$ is below 0.5, the polymer should be soluble if amorphous and linear.

- When $\chi_1$ equals 0.5, as in the case of the polystyrene–cyclohexane system at 34°C, then the Flory $\Theta$ conditions exist.

- If the polymer is crystalline, as in the case of polyethylene, it must be heated to near its melting temperature, so that the total free energy of melting plus dissolving is negative.

- For very many nonpolar polymer–solvent systems, $\chi_1$ is in the range of 0.3 to 0.4.

MOLECULAR WEIGHT AVERAGES

- There are four molecular weight averages in common use;
  - number-average molecular weight, $M_n$;
  - weight-average molecular weight, $M_w$;
  - $z$-average molecular weight, $M_z$;
  - viscosity-average molecular weight, $M_v$.

- $N_i$: the numbers of molecules having molecular weights $M_i$
- $w_i$: the weight of species with molecular weights $M_i$

- The quantity $a$ in the last equation varies from 0.5 to 0.8
For a random molecular weight distribution, such as produced by many free radical or condensation syntheses, $M_n : M_w : M_z = 1:2:3$.

An absolute method of measuring the molecular weight is one that depends solely on theoretical considerations, counting molecules and their weight directly.

Absolute methods of determining the number-average molecular weight include osmometry and other colligative methods, and end-group analysis.

Light-scattering yields an absolute weight-average molecular weight.

The relative methods require calibration based on an absolute method and include intrinsic viscosity and gel permeation chromatography (GPC).
DETERMINATION OF THE NUMBER-AVERAGE MOLECULAR WEIGHT

- The number-average molecular weight, $M_n$, involves a count of the number of molecules of each species, $N_i M_i$, summed over $i$, divided by the total number of molecules.

- There are two important groups of methods for determining $M_n$: End-Group Analyses and Colligative Properties.

End-Group Analyses

- The first group of methods involves end-group analyses. Many types of syntheses leave a special group on one or both ends of the molecule, such as hydroxyl and carboxyl.

- These can be titrated or analyzed instrumentally by such methods as infrared.

- For molecular weights above about 25,000 g/mol, however, the method becomes insensitive because the end groups are present in too low a concentration.

\[ M_n = \frac{C}{n} N_A \]
Colligative Properties

- Colligative properties depend on the number of molecules in a solution, and **not** their chemical constitution.
- The colligative properties include boiling point elevation, melting point depression, vapor pressure lowering, and osmotic pressure.
- The basic equations for the first two may be written

\[ \lim_{c \to 0} \frac{\Delta T_b}{c} = \frac{RT^2}{\rho \Delta H_v} \left( \frac{1}{M_n} \right) \]

\[ \lim_{c \to 0} \frac{\Delta T_f}{c} = -\frac{RT^2}{\rho \Delta H_f} \left( \frac{1}{M_n} \right) \]

where \( \Delta T_b \) and \( \Delta T_f \) are the boiling point elevation and freezing point depression, respectively; \( \rho \) is the solvent density; \( \Delta H_v \) and \( \Delta H_f \) are the latent heats of vaporization and fusion per gram of solvent, and \( c \) is the solute concentration in g/cm³.

Colligative Properties

- The osmotic pressure \( \pi \) depends on the molecular weight as follows

\[ \lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{M_n} \]

- Only osmotic pressure is large enough for fruitful studies at this molecular weight or higher.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor pressure lowering</td>
<td>( 4 \times 10^{-3}) mm Hg</td>
</tr>
<tr>
<td>Boiling point elevation</td>
<td>( 1.3 \times 10^{-3}) C</td>
</tr>
<tr>
<td>Freezing point depression</td>
<td>( 2.5 \times 10^{-3}) C</td>
</tr>
<tr>
<td>Osmotic pressure</td>
<td>15 cm solvent</td>
</tr>
</tbody>
</table>
Osmotic Pressure

- **Thermodynamic Basis**
  - Polymer solutions exhibit osmotic pressures because the chemical potentials of the pure solvent and the solvent in the solution are unequal.

  - Because of this inequality, there is a net flow of solvent, through a connecting membrane, from the pure solvent side to the solution side.

  - When sufficient pressure is built up on the solution side of the membrane, so that the two sides have the same activity, equilibrium will be restored.

Osmometry

- An analogy exists between osmotic pressure equation and the ideal gas law:

  \[ \lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{M_n} \sim PV = nRT \]

  - where \( n \) is in moles, as usual. The quantity \( n/V \) is equal to \( c/M \).

- **Instrumentation**
  - A typical static osmometer design includes a membrane that permeates only the solvent, a capillary, and a reference capillary.
Osmometry

- Typical membranes are made from regenerated cellulose or other microporous materials.
- Such an instrument usually requires 24 h to reach equilibrium.
- Since several concentrations usually need to be run, the time required to determine a molecular weight by osmometry has been reduced from a week to a few hours by these automatic instruments.

\[
\pi = -\frac{RT}{V_1} \left[ \ln(1 - v_2) + \left( 1 - \frac{1}{x} \right) v_2 + \chi v_2^2 \right]
\]

\[
\frac{\pi}{c} = RT \left( \frac{1}{M_n} + A_2 c + A_3 c^2 + \cdots \right)
\]

Osmometry

- Interactions between one polymer molecule and the solvent result in the second virial coefficient, \( A_2 \).
- *Multiple polymer–solvent interactions produce* higher virial coefficients, \( A_3, A_4, \) *and so on*.
- For medium molecular weights, the slope is substantially linear below about 1% solute concentration. Of course, \( A_2 = 1/M_n \).
Osmometry

- The quantity $A_2$ depends on both the temperature and the solvent, for a given polymer.

- The temperature at which $A_2$ equals zero is called the Flory $\Theta$-temperature. In this state, $\pi/c$ is independent of concentration, so that only one concentration need be studied to determine $M_n$.

- Since it is also the state where an infinite molecular weight polymer just precipitates and $\chi_\ell = 0.5$, considerable care must be taken to keep the polymer in solution.

---

Osmometry

- the determination of the Flory $\Theta$-temperature for cellulose tricaproate dissolved in dimethylformamide.
Osmometry

It must be emphasized that molecular weights determined by any of the colligative properties, osmometry in particular, are absolute molecular weights; that is, the values are determined by theory and not by prior calibration.

The practical limit of osmometry is about 500,000 g/mol because the pressures become too small.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Polybutadiene</td>
<td>n-Heptane</td>
<td>-1</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Biphenyl</td>
<td>125</td>
</tr>
<tr>
<td>Poly(n-butyl acrylate)</td>
<td>Benzene/methanol 52/48</td>
<td>25</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Cyclohexane</td>
<td>34</td>
</tr>
<tr>
<td>Poly(oxytetramethylene)</td>
<td>Chlorobenzene</td>
<td>25</td>
</tr>
<tr>
<td>Cellulose tricaproate</td>
<td>Dimethylformamide</td>
<td>41</td>
</tr>
</tbody>
</table>


WEIGHT-AVERAGE MOLECULAR WEIGHTS AND RADII OF GYRATION

The principal method of determining the weight-average molecular weight is light-scattering, although small-angle neutron scattering is now becoming important, especially in the bulk state, and X-ray scattering is also sometimes employed.

Light, like all other kinds of electromagnetic radiation interacts with matter in two ways:

1. Absorption: the photons (the light) disappear
2. Scattering: the photons change their direction
Scattering

The transmitted light is weakened by either absorption (top) or by scattering (bottom).

$\frac{x}{2}$

We can’t see the laser beam. At least not if the laser emits its beam in a room where the air is totally clean, i.e. dust free. When we see a laser beam we actually see photons being scattered on dust particles along the path of the beam.
Light scattering

- The basic equations used in light-scattering of polymer solutions today were developed by Debye and Zimm.

- The final result relates the observed light-scattering intensity to the osmotic pressure, $\pi$, of the polymer as follows:

$$\frac{Hc}{R(\theta)} = \frac{1}{RT} \left( \frac{\partial \pi}{\partial c} \right)_T$$
Light scattering

\[ \frac{HC}{R(\theta)} = \frac{1}{RT} \left( \frac{\partial \pi}{\partial c} \right)_T \]

- \( R(\theta) \) is called Rayleigh’s ratio and is equal to \( I_0 w^2/I_0 V_s \) where \( I_0 \) represents the light intensity observed at angle \( \theta \) scattered from a volume \( V_s \), if the distance from the source is \( w \) and the intensity of the incident light is \( I_0 \).

Light scattering

- The optical constant \( H \) is given by
  \[ H = \frac{2\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda^4} \]

  - \( n_0 \): the refractive index at wavelength \( \lambda \), \( N_A \): Avogadro’s number, \( \pi_1 = 3.14 \).

- The quantity \( dn/dc \) must be determined for each polymer–solvent pair. Then \( H \) is a constant for a particular polymer and solvent, determined experimentally.
Scattering Theory and Formulations

- The basic equation for the molecular weight and size for all three modes of scattering (light, neutron and X-ray) formulated by Debye can be written

\[
\frac{Hc}{R(\theta) - R(\text{solv})} = \frac{1}{M_w P(\theta)} + 2 A_2 c
\]

- This equation corrects \(R(\theta)\) for the solvent scattering.
- \(P(\theta)\) is the scattering form factor

If the particles are very small compared to the wavelength of the radiation (e.g., gas molecules), \(P(\theta)\), the scattering form factor, equals unity.

For particles (or molecules) larger than about 0.05 times the wavelength, \(P(\theta)\) differs from unity.
Scattering Theory and Formulations

- The quantity $P(\theta)$ is called the *single chain form factor*, which describes the angular scattering arising from the conformation of an individual chain.

In the Guinier region, $P(\theta)$ becomes a measure of the radius of gyration, $R_g$.

For a random coil, $P(\theta)$ is expressed by:

$$P(\theta) = \frac{2}{R_g^4 K^4} \left[ R_g^2 K^2 - [1 - \exp(-R_g^2 K^2)] \right]$$
Scattering Theory and Formulations

- The region of very small angles, $K^2 R_g^2 < 1$, is known as the Guinier region.

$$K = \frac{4\pi I}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

- The quantity $\lambda$ represents the wavelength of the radiation, and $\theta$ is the angle of scatter. The quantity $K$, sometimes written $q$ or $Q$, is called the wave vector.

Scattering Theory and Formulations

- The Appropriate Angular Range

$$K^2 R_g^2 < 1$$

- For ordinary-size polymer molecules, $R_g$ is of the order of 100 to 200 Å.
- For light-scattering $\theta$ is usually measured in the range of 45 to 135°, because $\lambda \approx 5000$ Å.
- For X rays ($\lambda \approx 1-2$ Å) and neutrons ($\lambda \approx 5$ Å), scattering measurements are usually made below 1°.

- The requirement of small angles for X-ray and neutron scattering has led to the construction of huge instruments. For example, X-ray scattering instruments may be 10 m long. The giant small-angle neutron scattering instruments are even 80 m long!
According to Zimm, the key equations at the limit of zero angle and zero concentration, respectively, relating the light-scattering intensity to the weight-average molecular weight $M_w$ and the average radius of gyration $R_g$, may be written

$$
\left( \frac{H - c}{R(\theta)} \right)_{\theta \to 0} = \frac{1}{M_w} + 2A_2c + \ldots
$$

$$
\left( H - c \right)_{c \to 0} = \frac{1}{M_w} \left[ 1 + \frac{1}{3} \left( \frac{4\pi}{\lambda^'} \right)^2 R_g^2 \sin^2 \frac{\theta}{2} + \ldots \right]
$$

$\lambda^'$ is the wavelength of the light in solution ($\lambda/n$).

Thus three quantities of interest can be determined from the same experiment:

- the weight-average molecular weight: $M_w$
- the average radius of gyration: $R_g$
- the second virial coefficient: $A_2$

A useful practical equation for the determination of $R_g$ from a plot of $H[c/R(\theta)]$ versus $\sin^2 \theta/2$ is

$$
R_g^2 = \frac{3(\lambda^')^2 \text{(initial slope)}}{16\pi_1^2 \text{(intercept)}}
$$
**Radius of gyration**

- The “radius of gyration”, $R_g^2$, is defined as the mean square distance away from the center of gravity for $N$ scattering points of distance $r_i$ from the center of gravity:

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} r_i^2$$

- For a random coil, it is related to the end-to-end distance, $r$, by

$$R_g^2 = \frac{r^2}{6}$$

- where $r$ is the distance between the ends of the chain. Different relationships hold for spheres, rods, and coils.

**The Zimm Plot**

- The following equations show the function $H[c/R(\theta)]$ in the limit of $\theta = 0$ and $c = 0$, respectively.

$$\left( \frac{H c}{R(\theta)} \right)_{\theta=0} = \frac{1}{M_w} + 2A_2c + \cdots$$

$$\left( \frac{H c}{R(\theta)} \right)_{c=0} = \frac{1}{M_w} \left[ 1 + \frac{1}{3} \left( \frac{4\pi}{\lambda^2} \right)^2 R_g^2 \sin^2 \frac{\theta}{2} + \cdots \right]$$

- To determine $M_w$, $R_g$ and $A_2$, a simple but laborious method of plotting the data could be used.
The Zimm Plot

• (a) shows a plot of $H[c/R(\theta)]$ versus concentration for the several angles extrapolated to $c = 0$. Part (b) is a replot of the intercepts from (a) versus $\sin^2(\theta/2)$, which yields $M_w$ and $R_g$.

\[ \frac{H_c}{R(\theta)} \]

\[ \frac{H_c}{R(\theta)} \bigg|_{c = 0} \]

\[ \sin^2(\theta/2) \]

\[ C \]

\[ 1/M_w \]

\[ R_g \]

• In (c), the same data as (a) are replotted, this time against $\sin^2(\theta/2)$ first. Then, in (d), the intercepts of (c) are plotted against concentration, yielding $M_w$ and $A_2$.

\[ \frac{H_c}{R(\theta)} \]

\[ \frac{H_c}{R(\theta)} \bigg|_{\theta = 0} \]

\[ \sin^2(\theta/2) \]

\[ 1/M_w \]

\[ A_2 \]
The Zimm Plot

• The intercepts from (b) and (d) must be equal, since they both equal 1/Mw. This last provides an internal test of the data.

• A most powerful advance was the introduction of the Zimm plot which enabled Mw, Rg and A2 to be calculated from a single master figure, by plotting H[c/R(θ)] versus a function of both angle and concentration.

• In a Zimm plot, the concentration is multiplied by an arbitrary constant divided out of the final answer.
Polymer Chain Dimensions and Random Coils

- Light-scattering studies show that for high enough molecular weight, polymer chains become random coils.

- During the 1940s and 1950s scientists theorized that the conformations of polymer chains in an amorphous bulk polymer are similar to that which exists under Flory $\theta$-conditions.

- When SANS instrumentation became available in the early 1970s, polymer scientists sought to reexamine chain conformation behavior, this time directly in the bulk amorphous state.

These studies confirmed that values of $(R_g^2/M_w)^{1/2}$ were substantially the same in the bulk as in Flory $\theta$-solvents.

The quantity $(R_g^2/M_w)^{1/2}$ is a measure of chain stiffness. For example, polycarbonate, with $(R_g^2/M_w)^{1/2} = 0.457$, is stiffer than polystyrene, which has a value of 0.275.

The importance of these quantities lies in their relation to physical and mechanical behavior. Both melt and solution viscosities depend directly on the radius of gyration of the polymer and on the chain’s capability of being deformed.
Both the colligative and the scattering methods result in absolute molecular weights; that is, the molecular weight can be calculated directly from first principles based on theory.

Frequently these methods are slow, and sometimes expensive.

In order to handle large numbers of samples, especially on a routine basis, rapid, inexpensive methods are required.

This need is fulfilled by intrinsic viscosity and by gel permeation chromatography (GPC).

Intrinsic Viscosity

Intrinsic viscosity measurements are carried out in dilute solution and result in the viscosity-average molecular weight.

Consider such a dilute solution flowing down a capillary tube.

The flow rate, and hence the shear rate, is different depending on the distance from the edge of the capillary.
Intrinsic Viscosity

- The solvent viscosity is $\eta_0$, usually expressed in poises, Stokes, or, more recently, Pascal seconds, Pa·s. The viscosity of the polymer solution is $\eta$.
- The relative viscosity is the ratio of the two

$$\eta_{rel} = \frac{\eta}{\eta_0}$$

- Of course, the relative viscosity is a quantity larger than unity. The specific viscosity is the relative viscosity minus one:

$$\eta_{sp} = \eta_{rel} - 1$$

Intrinsic Viscosity

- Usually $\eta_{sp}$ is a quantity between 0.2 and 0.6 for the best results.
- The specific viscosity, divided by the concentration and extrapolated to zero concentration, yields the intrinsic viscosity

$$\left[ \frac{\eta_{sp}}{c} \right]_{c=0} = [\eta]$$

- For dilute solutions, where the relative viscosity is just over unity, the following algebraic expansion is useful

$$\ln \eta_{rel} = \ln(\eta_{sp} + 1) \approx \eta_{sp} - \frac{\eta_{sp}^2}{2} + \cdots$$
Intrinsic Viscosity

- Then, dividing $\ln \eta_{rel}$ by $c$ and extrapolating to zero concentration also yields the intrinsic viscosity

$$\left[ \frac{\ln(\eta_{rel})}{c} \right]_{c=0} = [\eta]$$

- Note that the intrinsic viscosity is written with $\eta$ enclosed in brackets. This is not to be confused with the plain $\eta$, which is used to indicate solution or melt viscosities.

- Two sets of units are in use for $[\eta]$. The “American” units are 100 cm$^3$/g, whereas the “European” units are cm$^3$/g.

The Equivalent Sphere Model

- Now consider a coiled polymer molecule as being impenetrable to solvent in the first approximation.
- A hydrodynamic sphere of equivalent radius $R_e$ will be used to approximate the coil dimensions.
- In shear flow, it exhibits a frictional coefficient of $f_0$. Then according to Stokes law,

$$f_0 = 6\pi \eta_0 R_e$$
The Equivalent Sphere Model

- The Einstein viscosity relationship for spheres may be written

\[
\frac{\eta - \eta_0}{\eta_0} = \eta_{sp} = 2.5 \left( \frac{n_2}{V} \right) V_e
\]

- \( V_e = \frac{4\pi}{3} Re^3 \) and \( n_2/V \) is the number of molecules per unit volume.
- The quantity \( n_2 V_e/V \) is the volume fraction of equivalent spheres. The viscosity of an assembly of spheres depends only on their volume fraction.

\[
\frac{n_2}{V} = \frac{c N_A}{M}
\]

- where \( c \) is the concentration and \( N_A \) is Avogadro’s number

\[\boxed{\left[ \frac{\eta_{sp}}{c} \right]_{c=0} = [\eta] = 2.5 \frac{N_A V_e}{M}}\]

- Note that

\[
\frac{V_e}{M} = \frac{4\pi}{3} \frac{R_e^3}{M} = \frac{4\pi}{3} \left( \frac{R_e^2}{M} \right)^{3/2} M^{1/2}
\]

\[R_e = R_{e0} \alpha\]

- where \( \alpha \) is the expansion of the coil in a good solvent over that of a Flory \( \theta \)-solvent.
The Equivalent Sphere Model

- The quantity $R_{e0}^2/M$ is roughly constant. According to Flory, the expansion of the coil increases with molecular weight for high molecular weights as $M^{0.1}$, yielding

$$[\eta] = 2.5 \frac{4\pi}{3} N_A \left( \frac{R_{e0}^2}{M} \right)^{3/2} M^{1/2} \alpha^3$$

The Mark–Houwink–Sakurada Relationship

- In the late 1930s and 1940s Mark, Houwink, and Sakurada arrived at an empirical relationship between the molecular weight and the intrinsic viscosity

$$[\eta] = KM^a$$

- where $K$ and $a$ are constants for a particular polymer–solvent pair at a particular temperature.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>$K \times 10^6$</th>
<th>$a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Polybutadiene</td>
<td>Benzene</td>
<td>30</td>
<td>33.7</td>
<td>0.15</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1-Chloronaphthalene</td>
<td>19.9</td>
<td>21.5</td>
<td>0.65</td>
</tr>
<tr>
<td>Poly(ethyl acrylate)</td>
<td>Acetone</td>
<td>25</td>
<td>51</td>
<td>0.95</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>Acetone</td>
<td>20</td>
<td>5.5</td>
<td>0.75</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>Benzene</td>
<td>30</td>
<td>22</td>
<td>0.65</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Butanone</td>
<td>25</td>
<td>39</td>
<td>0.95</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Cyclohexane (#-solvent)</td>
<td>34.5</td>
<td>84.6</td>
<td>0.90</td>
</tr>
<tr>
<td>Polytetrahydrofuran</td>
<td>Toluene</td>
<td>26</td>
<td>25.1</td>
<td>0.75</td>
</tr>
<tr>
<td>Polytetrahydrofuran</td>
<td>Ethyl acetate hexane (#-solvent)</td>
<td>31.8</td>
<td>206</td>
<td>0.49</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>Acetone</td>
<td>25</td>
<td>6.93</td>
<td>0.91</td>
</tr>
</tbody>
</table>
The Mark–Houwink–Sakurada Relationship

- The weight-average molecular weights of sharp fractions or narrow molecular weight distributions are usually substituted to determine $K$ and $a$.
- The value of $a$ is predicted to vary from 0.5 for a Flory $\theta$-solvent to about 0.8 in a thermodynamically good solvent.
- This corresponds to $a$ increasing from a zero dependence on the molecular weight to a 0.1 power dependence. More generally, it should be pointed out that $a$ varies from 0 to 2.

<table>
<thead>
<tr>
<th>$a$</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Spheres</td>
</tr>
<tr>
<td>0.5–0.8</td>
<td>Random coils</td>
</tr>
<tr>
<td>1.0</td>
<td>Stiff coils</td>
</tr>
<tr>
<td>2.0</td>
<td>Rods</td>
</tr>
</tbody>
</table>

- The quantity $K$ is often given in terms of the universal constant $\Phi$.

$$K = \Phi \left( \frac{\overline{R^2}}{M} \right)^{3/2}$$

- Where $\overline{R^2}$ represents the mean square end-to-end distance of the unperturbed coil.
- If the number-average molecular weights are used, then $\Phi$ equals $2.5 \times 10^{21}$ dl/mol·cm$^3$. A theoretical value of $3.6 \times 10^{21}$ dl/mol·cm$^3$ can be calculated from a study of the chain frictional coefficients.
- For many theoretical purposes, it is convenient to express the Mark–Houwink–Sakurada equation in the form

$$[\eta] = \Phi \left( \frac{\overline{R^2}}{M} \right)^{3/2} M^{1/2} \alpha^3 = KM^{1/2} \alpha^3$$
The Mark–Houwink–Sakurada Relationship

• If the intrinsic viscosity is determined in both a Flory θ-solvent and a “good” solvent, the expansion of the coil may be estimated. From equation

\[ \frac{[\eta]}{[\eta]_\theta} = \alpha^3 \]

• Values of \( \alpha \) vary from unity in Flory θ-solvents to about 2 or 3, increasing with molecular weight.

Intrinsic Viscosity Experiments

• In most experiments, dilute solutions of about 1% polymer are made up. The quantity \( \eta_{\text{rel}} \) should be about 1.6 for the highest concentration used. The most frequently used instrument is the Ubbelhode viscometer.

The Ubbelhode viscometer

Ubbelhode viscometer
Intrinsic Viscosity

1. Both lines must extrapolate to the same intercept at zero concentration.

2. The sum of the slopes of the two curves is related through the Huggins equation,

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

and the Kraemer equation,

\[
\frac{\ln \eta_{rel}}{c} = [\eta] - k''[\eta]^2 c
\]

Should be

\[k' + k'' = 0.5\]
Intrinsic Viscosity

- If either of these requirements is not met, molecular aggregation, ionic effects, or other problems may be indicated.
- For many polymer–solvent systems, $k'$ is about 0.35, and $k''$ is about 0.15.
- In order to determine the constants $K$ and $a$ in the Mark–Houwink–Sakurada equation, a double logarithmic plot of molecular weight versus intrinsic viscosity is prepared.

![Intrinsic Viscosity Graph]

Example Calculation Involving Intrinsic Viscosity

- we are interested in a fast, approximate molecular weight of a polystyrene sample. We dissolve 0.10 g of the polymer in 100 ml of butanone and measure the flow times at 25°C in an Ubbelhode capillary viscometer. The results are

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure butanone</td>
<td>110</td>
</tr>
<tr>
<td>0.10% Polystyrene solution</td>
<td>140</td>
</tr>
</tbody>
</table>

\[
\eta_{rel} = \frac{\eta}{\eta_0} = \frac{140}{110} = 1.273
\]
\[
\eta_{sp} = \eta_{rel} - 1 = 0.273
\]
\[
\eta_{exp} = \frac{0.273 \text{ ml/g}}{0.001} = 2.73 \times 10^2 \text{ ml/g}
\]
Example Calculation Involving Intrinsic Viscosity

- As an approximation, assume that the concentration is near zero, and the $[\eta] = 2.73 \times 10^2$ ml/g.

- Using the Mark–Houwink–Sakurada relation, equation

\[
[\eta] = K M_V^p \\
2.73 \times 10^2 = 39 \times 10^{-3} M_V^{0.58} \\
M_V = 4.26 \times 10^6 \text{ g/mol}
\]

GEL PERMEATION CHROMATOGRAPHY (GPC)

- Gel permeation chromatography (GPC), sometimes called size exclusion chromatography, SEC, makes use of the size exclusion principle.

- The size of the molecule, defined by its hydrodynamic radius, can or cannot enter small pores of the stationary phase.

- The smaller molecules diffuse in and out of the pores via Brownian motion and are delayed. The larger molecules pass by and continue in the mobile phase.
Gel Permeation Chromatography (GPC)

- The stationary phase consists of small, porous particles. While the mobile phase flows at a specified rate controlled by the solvent delivery system, the sample is injected into the mobile phase and enters the columns.

- A detector (like differential refractometer (RI)) monitors the separation and responds to components as they elute from the column.

The length of time that a particular fraction remains in the columns is called the retention time.
Gel Permeation Chromatography (GPC)

- **The Universal Calibration**
  
  Beginning with the Mark–Houwink–Sakurada relationship, it is easy to show that the average molecular size is given by

\[
[\eta]M = \Phi \left( \frac{r_0^2}{\alpha} \right)^{3/2}
\]

- The right-hand side is proportional to the polymer’s hydrodynamic volume.

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The Universal Calibration

- A new aspect of GPC calibration arises from the recognition that a polymer’s hydrodynamic volume might form the basis for molecular weight determination.

- Since GPC depends on the hydrodynamic volume rather than its molecular weight, a new calibration method is suggested.

- This is the “universal calibration,” which calls for a plot of [\eta]M versus elution volume.

- Universal calibration can be done if the Mark-Houwink parameters are known for the polymer samples in the same solvent and at the same temperature.
The Universal Calibration

The universal calibration is valid for a range of topologies and chemical compositions. However, it cannot be used for highly branched materials or polyelectrolytes, which have different or varying hydrodynamic volume relationships.

SOLUTION THERMODYNAMICS AND MOLECULAR WEIGHTS

- A knowledge of solution thermodynamics is critically important in determining the suitability of a solvent for a molecular weight determination.

- Once having decided on a suitable solvent, solution thermodynamics provides a basis for determining how an extrapolation to zero concentration is to be carried out.

- Below the Flory \( \Theta \)-temperature, polymer solutions may phase-separate.
The Flory $\theta$-temperature is defined by several different criteria:

1. It is the temperature where $A_2$ is zero for dilute solutions, and $\chi_1 = 0.5$
2. It is the temperature where the radius of gyration approximates that of the bulk polymer
3. It is the temperature at which an infinite molecular weight fraction would just precipitate

The molecular weight and polydispersity of polymers remain among the most important properties that are measured.

The methods are divided into absolute methods, which determine the molecular weight from first principles, and relative methods, which depend on prior calibration.

The latter are usually selected because they are fast and inexpensive.
SOLUTION THERMODYNAMICS AND MOLECULAR WEIGHTS

- The low-molecular-weight component behaves substantially as a plasticizer, weakening the material rather than strengthening it.

- The high-molecular-weight tail adds much to the melt viscosity, since the melt viscosity of high-molecular-weight polymers depends on $M_w$ to the 3.4 power

Table 3.15  Summary of molecular weight methods and results

<table>
<thead>
<tr>
<th>Method</th>
<th>Absolute</th>
<th>Relative</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel permeation chromatography</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>Molecular-weight</td>
</tr>
<tr>
<td>Scattering—light, neutrons</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>$R_g, A_2$</td>
</tr>
<tr>
<td>Osmometry</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>$A_2$</td>
</tr>
<tr>
<td>Intrinsic viscosity [$\eta$]</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>$M_c$</td>
</tr>
</tbody>
</table>