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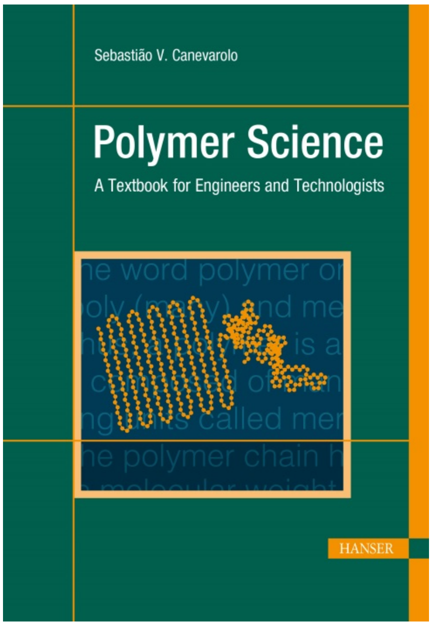

Sample Pages

Polymer Science

Sebastião V. Canevarolo Jr.

ISBN: 978-1-56990-725-2

E-Book ISBN: 978-1-56990-726-9

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Preface

The idea of writing this book was to create a reference for the undergraduate and graduate students of polymer science in the Materials Engineering course of the Federal University of São Carlos, Brazil, where I have been lecturing for the past four decades. During this period much has been developed and discovered in the area of synthesis and technology of polymer materials. Despite all this frenetic development, the fundamental concepts discussed here, defined mainly by the great researchers in polymer science – Staudinger and Carothers in the 1920s, Ziegler and Natta in the 1950s, and Flory, to name a few – have remained constant because by being general they have the greatness of universality. Deeply understanding concepts such as degree of crystallinity, melting and glass transition temperature, and mechanical behavior and applying them to our needs has made it possible to scientifically solve the everyday problems polymer engineers face. I hope the way I set and discuss the basic concepts of the plastics world may help you too to tackle your everyday problems. Read it unhurriedly, reflect on each concept, go beyond the text itself, give wings to your logical imagination; this will give you confidence in the basic fundamentals of the ever-increasing modern commodity that plastics have become.

To better discuss the matters, I included in every chapter some problems and presented their solution. I hope that I have chosen examples that are sufficiently comprehensive and representative. More important than this, I hope the answers I have proposed are a way of showing the reader how to tackle the problem and solve it. At the end of each chapter a list of exercises was added, with the main intention of testing the clarity with which the concepts covered were understood by the reader, helping to assimilate each one of them in the best possible way.

I hope this text is light, having a minimum number of words, only those necessary to express the idea well. On the other hand, I would like it to be faithful to what many bright and tireless researchers thought, tested, and, after verifying that their ideas made sense, shared with us. A light text only in its approach, but dense in concept, indeed, as every textbook should be.

Thanks for choosing it and good reading.

S. V. Canevarolo

São Carlos, Brazil

October 2019

About the Author

Sebastião Vicente Canevarolo was born on 30/May/1956 in São Carlos, SP, Brazil. In 1978, he finished the undergraduate course of Materials Engineering in the Department of Materials Engineering of the Federal University of São Carlos (UFSCar), joining immediately this same department as a lecturer, and is currently still working there.

He completed the Master's Program in Materials Engineering at UFSCar in 1982 and got his Ph.D. at the Institute of Polymer Technology at Loughborough University of Technology, England in 1986. He carried out a postdoctoral program at the Dipartimento di Ingegneria Chimica ed Alimentare of the University of Salerno, Italy from Jun/93 to Jul/94, and is a Researcher Fellow of CNPq (Brazilian National Council for Scientific and Technological Development) since 1994 and Full Professor at UFSCar since 2015.

In different periods, he has been the Vice-Head of DEMa (http://www.dema.ufscar.br), Supervisor of the Polymer Laboratories, Coordinator of the Polymer Group, member of the Department Council, Head of the Graduate Program in Science and Materials Engineering (http://www.ppgcem.ufscar.br), founder and for 20 years Director of the Brazilian Polymer Association, ABPol (http://www.abpol.com.br), Editor-in-Chief of the Brazilian polymers journal *Polímeros: Ciência e Tecnologia* (ISSN 1678-5169 and 0104-1428, www.revistapolimeros.org.br), honorary member of the Brazilian Association of Thermal Analysis and Calorimetry-ABRATEC, and member of the Editorial Board of Materials Research (http://www.materialsresearch.org.br). He has participated in the organizing committee of various congresses in the polymer area in Brazil (XIICBECIMAT, 4CBPol, 1CBRATEC, 1SBE, 9CBPol, 11CBPol) and abroad (PPS-18, Portugal).

His research field is developing optical techniques to characterize in real time (in-line) the extrusion process, constructing the hardware (slit-die, optical cell, in-line turbidimeter, in-line rheo-polarimeter, in-line colorimeter, in-line LALLS), and developing the software (in LabView). He has two patent applications, published one chapter in an English-language book and two Portuguese-language books: *Ciência dos Polímeros*, ISBN 85-88098-10-5, 2010, and *Técnicas de Caracterização de Polímeros*, ISBN 85-88098-19-9, 2004, both from Artliber. The first one has become a standard reference in the area, being used as bibliographic source for all Brazilian undergraduate and graduate polymer courses, and its content is the basis for this book.

Canevarolo has published 55 original papers in international journals, 17 in Brazilian journals, and participated in presenting 130 articles in national and international congresses. He has given 23 invited conferences in national and international events, supervised three postdoc researches, nine Ph.D. theses, and 29 Master theses. He has participated in the CNPq PRONEX project and the FAPESP Thematic Program, coordinates an international cooperation agreement between Brazil and Portugal, and is the Brazilian National Representative in the Polymer Processing Society (PPS). Currently, he is Full Professor at DEMa/UFSCar and Research Fellow from CNPq PQ-2. He has an h-index of 13, with 775 citations.

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Foreword

Dear reader, if you are in any way involved with plastic materials and looking for a direct but not superficial text, deep but easy to understand, rich in information without being boring, I believe this is the book that you were looking for. Read it once or twice and have it on hand for a quick look: its figures, charts, tables, and appendices have been prepared not only to illustrate the text but mainly to be accessed when necessary. An efficient and productive professional is not one who knows by heart hundreds of phone numbers but the one who knows where to find them.

In its over 350 pages, *Polymer Science: A Textbook for Polymer Engineers* tries to summarize in a didactic way the vast field of knowledge that was developed in the twentieth century in the area of polymers. Better known as plastics, these new materials started their lives in a timid way but quickly gained their space due to both their superior performance and the acceptance of the increasingly demanding consumers. Their low price, light weight, easy molding, good chemical, thermal, and mechanical resistance, easy coloring, and great functionality, permitting the production of goods with complicated shapes, are the reason for their total acceptance by the modern designer. All these characteristics, almost gifted, are not obtained for free. It is necessary that the technician/engineer who is choosing knows their particularities deeply so that the choice is not a “shot in the foot”. This book attempts to provide practitioners who are in some way involved with polymer materials, whether in obtaining, selecting, or molding, technical/scientific information that will enable them to act knowingly. The empirical method of trial and error has no place in the twenty-first century; professionals with decision-making power have to be aware of the basic fundamentals, their intricacies, and implications.

Finally, the purpose of this book is to give you technical knowledge about the vast and economically attractive field of plastic materials. It is easy to remember that having the information, not necessarily known by heart but definitely within reach, is what counts. Good reading and good business!

S. V. Canevarolo

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3

Polymers in Solution

3.1 Technological Importance

For formulation, production, and quality control in the paint, varnish, and adhesive industries, it is necessary to obtain stable solutions (which do not undergo major changes in viscosity with storage time), with safe handling (the use of flammable solvents should be avoided if possible) at a competitive cost (an expensive solvent may be replaced by a mixture of other organic liquids to produce a thinner with the power to solubilize the solids). That is, what is the best thinner (or mixture of solvents) to solubilize a given formulation (or mixture of polymers)?

The melt viscosity shown by a polymer while being processed is due to the difficulty polymer chains face to change conformation during flow. This difficulty is created by the large number of entanglements, formed among the long polymer chains. Thus, it is important to know and control the average molecular weight obtained during the polymerization. The molecular weight is an average of the length (or weight) of all chains measured individually. For this measurement, it is necessary to separate the chains, which can be done in a practical manner by solubilizing the polymer in a suitable solvent.

3.2 Conformation of the Polymer Chain in Solution

The conformation of a polymer chain defines the spatial geometric arrangement of the atoms forming the molecule. This arrangement can undergo many spatial changes as long as the carbon tetrahedral geometry is maintained. This usually occurs by rotation of single covalent C–C bonds, keeping the distance and the angle of the bonds fixed. Despite these two constraints, there are a large number of positions in which the carbon atoms of the main chain can place themselves, since all points in the cone defined by the equidistant locus of the previous carbon atom by a fixed distance (bond length) forming a fixed angle (bond angle) can be used. Figure 3.1 shows a schematic representation of a polymeric chain in solution when subjected to a change in temperature or solvent power.

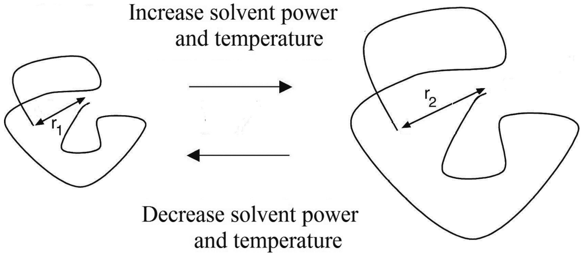


Figure 3.1 Schematic representation of the change in the volume occupied by a polymer chain in solution and its end-to-end chain distance when subjected to a change in temperature or solvent power

The most stable conformation in solution is the random coil conformation. In the presence of a good solvent and/or high temperatures, the hydrodynamic volume occupied by the polymer chain increases. Likewise, in the presence of a poor solvent and/or low temperatures, the volume occupied by the molecule in solution tends to decrease. A practical way to quantify the hydrodynamic volume size is by estimating the geometric mean distance between the chain ends. For this purpose, the square root of the mean squares of the distances between chain ends is calculated as:

$$\bar{r} = \left(\overline{r^2}\right)^{1/2} \tag{3.1}$$

In an attempt to calculate the average distance between the two ends of a chain, several theoretical models were developed by Prof. Paul John Flory (19/Jun/1910–9/Sep/1985), physicochemical professor at Stanford University, California, USA, Nobel prize in chemistry of 1974, with different levels of detail. The most known are:

3.2.1 Free Joined Chain Model

This is the simplest model where it is assumed that the chain is formed by a sequence of bars with a fixed length (l) connected by the tips without restriction of the angle formed between them. This model can also be seen as that of a Brownian movement or “the walking drunk man”. In this case, the mean square distance that the drunkard will walk after n steps with fixed length l will be:

$$\bar{r} = \left(\overline{r^2}\right)^{1/2} = l\sqrt{n} \tag{3.2}$$

Figure 3.2 shows a possible conformation of a polymer chain obtained from a numerical simulation using random bond angles (open points). The simulation took 100 single C–C bonds with unit bond length, following the predicted freely joined chain model. This model is two-dimensional and does not take into account short- and long-range interactions. This allows the crossing of two segments, something that is impossible in reality, making a much more closed conformation than the real one. In any case, it serves as a starting point in the development of other simulations, presenting results that are closer to reality.

3.2.2 Free Tetrahedral Rotation Chain Model

If the bond angle is set as fixed, the constraint increases and the mean square distance between the chain ends becomes:

$$\bar{r} = \left(\overline{r^2}\right)^{1/2} = 1\sqrt{n}\left[\frac{1-\cos\theta}{1+\cos\theta}\right]^{1/2} \tag{3.3}$$

which, in the case of the carbon–carbon single bond, reduces to:

$$\bar{r} = \left(\overline{r^2}\right)^{1/2} = 1\sqrt{2n} \tag{3.4}$$

The tetrahedral angle $\theta = 109°\ 28'$ then $\cos\theta = -1/3$. This results in a mean square distance of the free tetrahedral rotation chain model 41% higher than the value calculated by the free joined chain model.

$$\left(\overline{r^2_{\text{tetrahedral}}}\right)^{1/2} = \sqrt{2}\left(\overline{r^2_{\text{random}}}\right)^{1/2} = 1.41\left(\overline{r^2_{\text{random}}}\right)^{1/2} \tag{3.5}$$

Figure 3.2 also shows the result of a simulation using the free tetrahedral rotation chain model (full points) for a chain with 100 C–C single bonds.

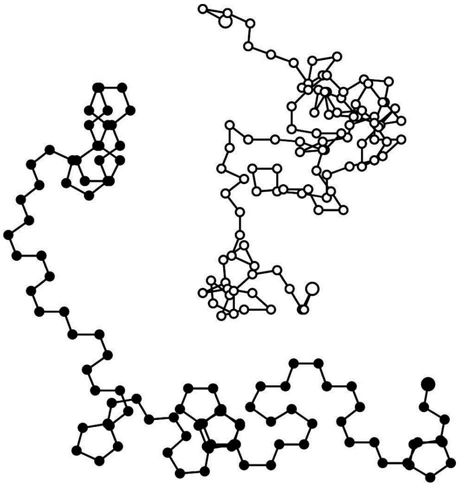


Figure 3.2 Conformations of a polymer chain according to the model of the free joined chain (open points) and with the free tetrahedral rotation chain (full points). Simulation with 100 C–C single bonds and unitary bond length. The restriction imposed at the C–C–C angle by the free tetrahedral rotation model creates a more expanded chain (with a higher hydrodynamic volume) and a larger quadratic mean distance between chain ends

3.2.3 Restricted Movement Chain Model

One can further restrict movement by considering that repulsion effects present in a given position will also be present on the other side of the molecule (action symmetry). Thus, the angle of rotation of the chain ϕ is defined as the angle the next carbon atom makes relative to the plane formed by the three carbon atoms prior to it in the chain. Figure 3.3 shows a diagram with the angle of rotation ϕ.

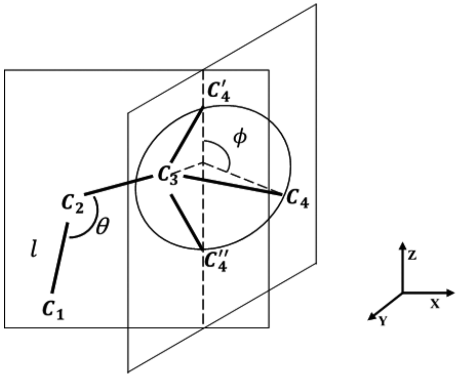


Figure 3.3 Diagram of a sequence of four single bonded carbon atoms showing the bond length l, bond angle θ, and the rotation angle ϕ

Solved problem 4.1

Calculate the densities of the orthorhombic and monoclinic crystalline phases of polyethylene.

Taking the top view of the *orthorhombic polyethylene unit cell* as shown in Figure 4.9b, it is possible to observe that it is formed of a quarter of a mer in each corner plus an integer mer in the center, that is, 4 × 1/4 + 1 = 2 mers/unit cell. A polyethylene mer contains 2 × C + 4 × H, i.e., it weighs 2 × 12 + 4 × 1 = 28 g/mol. Then we can calculate the density of the orthorhombic unit cell of polyethylene, which is equal to the density of the crystal or crystalline phase, by:

$$\rho = \frac{m}{v} = \frac{2 \times \dfrac{28\text{ g.mol}}{\text{mer}} / 6.02 \times 10^{23}\text{mers / mol}}{7.42\,\text{Å} \times 4.95\,\text{Å} \times 2.55\,\text{Å}\ \left(10^{-8}\text{cm / Å}\right)^3} = 0.993\text{ g/cm}^3$$

This value is very close to the experimental value of 1.011 g/cm^3, with an error of only −1.8%.

The calculation using the *monoclinic unit cell* follows the same methodology, using Figure 4.9c. The unit cell forms the geometric figure of a trapeze that has as its area:

$$A_{\text{UC monoclinic}} = \text{Base} \times \text{Height} = \text{side a} \times \left(\text{side b} \times \sin 72.1°\right)$$

$$= 8.09 \times \left(4.79 \times 0.9516\right) = 36.87\,\text{Å}^2$$

It is also formed from a quarter of a mer in each corner plus half a mer on each side, that is, 4 × 1/4 + 2 × 1/2 = 2 mers/unit cell.

$$\rho = \frac{m}{v} = \frac{2 \times \dfrac{28\text{ g.mol}}{\text{mer}} / 6.02 \times 10^{23}\text{mers / mol}}{36.87\,\text{Å} \times 2.55\,\text{Å} \times \left(10^{-8}\text{cm / Å}\right)^3} = 0.989\text{ g / cm}^3$$

Solved problem 4.2

Calculate the number of PE chains required to produce a 100 nm (1000 Å) diameter fibril. Assume an orthorhombic unit cell (UC).

We start by calculating the number of PE chains per unit cell:

$$\frac{\text{no. of chains}}{\text{UC}} = 4\frac{1}{4} + 1 \times 1 = 2\text{ chains / UC}$$

The area of a UC is: $A_{\text{cross UC}} = a \times b = 7.42 \times 4.95 = 37.5\,\text{Å}^2$

The cross-sectional area of a fibril is: $A_{\text{fibril}} = \dfrac{\pi D^2}{4} = \dfrac{\pi\left(1000\,\text{Å}\right)^2}{4} = 7.85 \times 10^5\,\text{Å}^2$

The number of UCs per fibril is: $n_{UC} = \frac{A_{\text{fibril}}}{A_{\text{cross UC}}} = 7.85 \times 10^5\,\text{Å}^2 / 37.5\,\text{Å}^2$

$n_{UC} = 20.933$

Finally, the number of PE chains per fibril is:

$n_{\text{chains per fibril}} = 2 \times 20.933 \cong 42.000$

4.6.2 Polypropylene (PP)

Isotactic polypropylene PPi has a monoclinic unit cell with the following unit cell parameters: $a = 6.65 \pm 0.05\,\text{Å}$; $b = 20.96 \pm 0.15\,\text{Å}$; $c = 6.50 \pm 0.04\,\text{Å}$; and angles $\alpha = \gamma = 90°$ and $\beta = 99°20'$. Figure 4.10 shows a view along the *c*-axis, i.e., the axis of the main chain. The circular arrows at the center of the chains indicate the direction of rotation of the helix and the fractional numbers next to the carbon atom of the side group $-CH_3$, its partial height inside the unit cell, counted from the basal plane, subdivided into 12 fractions.

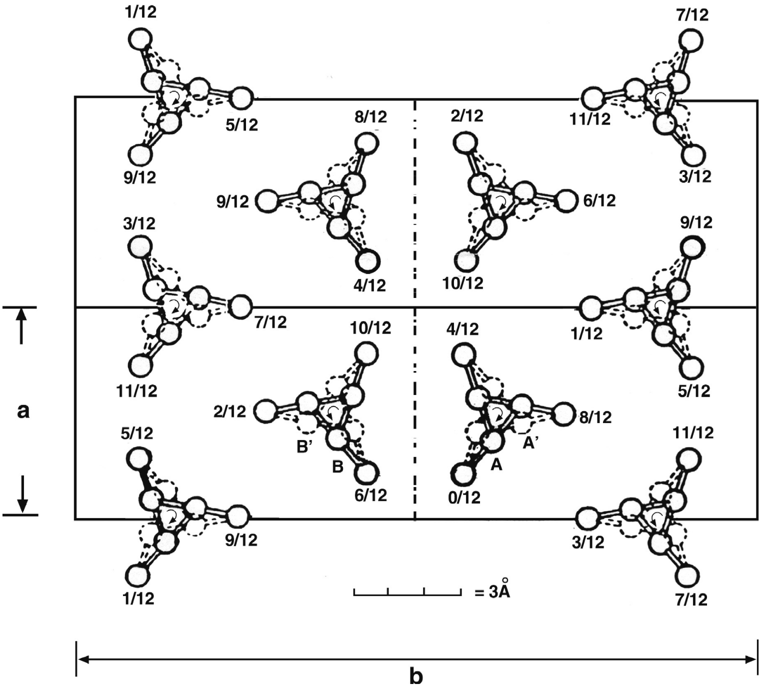


Figure 4.10 Projection of the monoclinic crystalline unit cell of the polypropylene seen along the *c*-axis, i.e., the main-chain axis

4.6.3 Polyhexamethylene Adipamide (Nylon 6,6)

The crystalline phase of nylon 6,6 may be present in at least three distinct crystallographic forms. At room temperature, the forms α and β are stable, both triclinic, with a planar zig-zag conformation. Figure 4.11 shows the unit cell of the α form. The γ form only appears at high temperatures and is not yet well defined.

The unit cell parameters of the α and β forms are:

α form		β form	
a = 4.9 Å	α = 48.5°	a = 4.9 Å	α = 90°
b = 5.4 Å	β = 77°	b = 8.0 Å	β = 77°
c = 17.2 Å	γ = 63.5°	c = 17.2 Å	γ = 67°

The hydrogen bond formed between the –NH and –C=O groups creates strong secondary intermolecular links, aligning the zig-zag planes of the layered chains where the bonding forces between the chain segments within each layer are greater than the intermolecular dispersion forces between the layers.

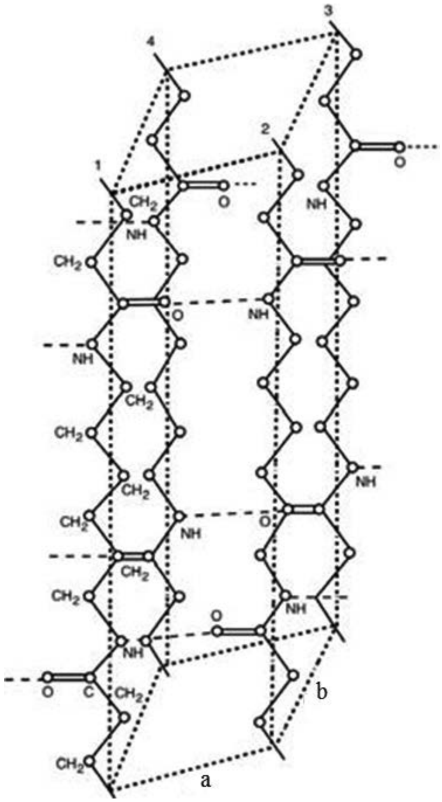


Figure 4.11 Triclinic unity cell of the α form of nylon 6,6

4.6.4 Polyethylene Terephthalate (PET)

The crystallization conformation of polyethylene terephthalate (PET) is planar zig-zag forming a triclinic unit cell with the following parameters: a = 4.56 Å; b = 5.94 Å; c = 10.75 Å and angles α = 98.5°; β = 118°; γ = 112°. To allow more packing, the terephthalic acid group makes a small angle with the axis of the polymer chain. Figure 4.12 shows several views of the PET unit cell.

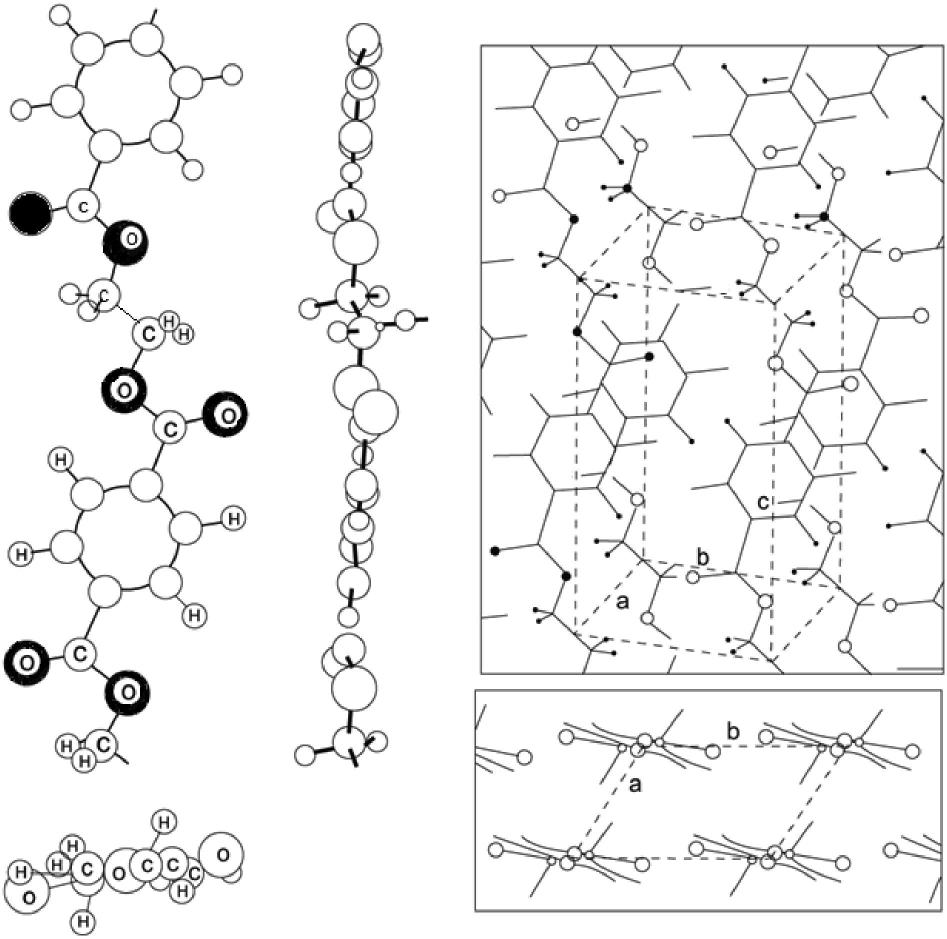


Figure 4.12 Planar zig-zag crystallization conformation of the PET chains and its triclinic unit cell

$$\overline{M_n} = \frac{\sum h_i}{\sum N_i} = \frac{390}{4.85 \times 10^{-3}} = 80.400 \text{ g/mol};$$

$$\overline{M_w} = \frac{\sum N_i \left(M_i\right)^2}{\sum h_i} = \frac{3.46 \times 10^7}{390} = 88.700 \text{ g/mol};$$

$$\overline{M_z} = \frac{\sum N_i \left(M_i\right)^3}{\sum N_i \left(M_i\right)^2} = \frac{3.83 \times 10^{12}}{3.46 \times 10^7} = 110.700 \text{ g/mol};$$

and the polydispersity $PD = \frac{\overline{M_w}}{\overline{M_n}} = \frac{88,700}{80,400} = 1.1$

6.5 Most Probable Molecular Weight Distribution Function

It is theoretically possible to predict the width of the molecular weight distribution depending on the type of polymerization reaction. Thus, polycondensation tends to produce mainly linear chains that grow with the polymerization reaction time. On the other hand, the chain polymerization will be dependent on its preferential type of termination mechanism.

6.5.1 Polycondensation with Linear Chains

The polycondensation reaction of two initial bifunctional materials yields a long linear chain where each component enters alternately during the chaining. This produces the so-called **most probable distribution function**. Assuming the reaction of a diacid (A) with a dialcohol (G, glycol) forms a linear polyester chain, as shown:

*n*A + *n*G → A-G-A-G-A-G-A-G-........-A-G

then if for the formation of this chain a total of x molecules of the reactants (half of the molecules of diacid and half of glycol) are used, then $x-1$ bonds are formed. Assuming that the probability of each of these esterification reactions to occur is p, also known as reaction extension, one can conclude that the probability of a molecule being formed with exactly x units is n_x given by:

$$n_x = p^{x-1}\left(1-p\right) \tag{6.25}$$

the first term relating to the probability that the same reaction (p) happens $x-1$ consecutive times, and the second term appears to ensure that the chain stops growing exactly after these $x-1$ reactions. Thus, the number of molecules (N_x) with a size of exactly x is the total number of molecules available (N) times their probability of existing n_x:

$$N_x = N \times n_x \tag{6.26}$$

or

$$N_x = N\left(1-p\right) \times p^{x-1} \tag{6.27}$$

but the total number of molecules available is the total number of unreacted molecules (N_0), i.e.,

$$N = N_0 \times \left(1-p\right) \tag{6.28}$$

Replacing these equations, the **number most probable molecular weight distribution function** is:

$$N_x = N_0 \times \left(1-p\right)^2 \times p^{x-1} \tag{6.29}$$

which can be converted into **weight function** by neglecting the loss of mass due to the elimination of molecules of low molecular weight after each condensation reaction (water in the case of formation of the ester bond).

$$w_x = x \times \frac{N_x}{N_0} \tag{6.30}$$

that is, obtaining the **weight most probable molecular weight distribution function** as:

$$w_x = x \times \left(1-p\right)^2 \times p^{x-1} \tag{6.31}$$

Figure 6.11a graphically shows the number most probable MWD function and Figure 6.11b shows the weight most probable MWD function, calculated for four probability values: $p = 0.90$, 0.96, 0.98, and 0.99. The higher the probability of the polymerization reaction, the greater the number of initial molecules that will react, generating larger chains and shifting the curves to the right. With the lowest probability, $p = 0.90 = 90\%$, the average number of reacted molecules, defined by the peak of the weight function, is only $x \cong 10$. By increasing the probability to $p = 0.96 = 96\%$, the average number of molecules that react to form the chain increases to $x \cong 25$, and if we reach $p = 0.99 = 99\%$, it increases even more to $x \cong 140$, the typical value of a commercial poly(ethylene terephthalate) PET polymer.

The **number average polymerization degree** ($\overline{x_n}$) can also be estimated as:

$$\overline{x_n} = \sum x \times n_x = \sum x \times p^{x-1} \times (1-p) = \frac{1}{1-p} \tag{6.32}$$

and in weight fraction ($\overline{x_w}$) as:

$$\overline{x_w} = \sum x \times w_x = \sum x \times x \times p^{x-1} \times (1-p) = \frac{1+p}{1-p} \tag{6.33}$$

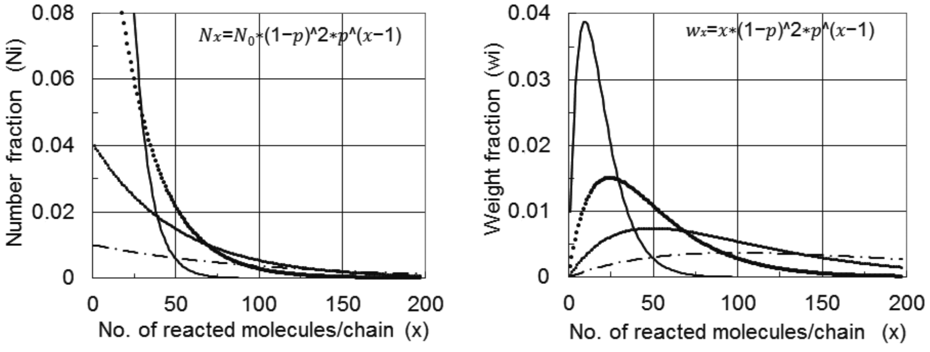
Thus, the width of the most probable MW distribution curve of a polycondensation with linear chain is:

$$\frac{\overline{x_w}}{\overline{x_n}} = 1+p \tag{6.34}$$

assuming $p \cong 1$, then one can say that

$$\frac{\overline{x_w}}{\overline{x_n}} \cong 2 \tag{6.35}$$

i.e., the polydispersity calculated for a polycondensation is approximately 2 (see Table 6.5). Nylons are polymers obtained by this type of polymerization and commercial products have $PD \cong 2$.



a) b)

Figure 6.11 (a) Number most probable MW distribution function and (b) weight most probable MW distribution function, simulated for four different reaction probabilities: $p = 0.90, 0.96, 0.98$, and 0.99

6.5.2 Chain Polymerization

This polymerization presents three types of preferential terminations:

6.5.2.1 Chain Transfer Termination

The hydrogen is transferred from the solvent molecule to the reactive growing chain end, terminating the polymerization. In this case, the most probable molecular weight distribution function can be applied, in the same way it was for the polycondensation or step polymerization. In order to synthesize a polyethylene with degree of polymerization $x = GP = 1000$, it is necessary that the probability of the ethylene addition reaction has at least 3 nines, that is, $p \geq 99.9\%$.

6.5.2.2 Combination Termination

In this case, two growing radical chains meet and react by forming a single covalent bond. The molecular weight of the final chain will be the sum of the initial two that formed it. In this case, the **distribution function** is narrower than the most probable:

$$w_x = \frac{x}{2}(x-1) \times (1-p)^3 \times p^{x-2} \tag{6.36}$$

6.5.2.3 Polymerization without Termination

This type of termination occurs specially in anionic polymerizations. The distribution function follows **Poisson's distribution**:

$$N_x = \frac{e^{-\nu} \times \nu^{(x-1)}}{(x-1)!} \tag{6.37}$$

and

$$w_x = \frac{\nu \times x \times e^{-\nu} \times \nu^{(x-2)}}{(\nu+1) \times (x-1)!} \tag{6.38}$$

v being the number of reacted monomers per polymer chain. The distribution width in the anionic polymerization is:

$$\frac{\overline{x_w}}{\overline{x_n}} = 1 + \frac{\nu}{(\nu+1)^2} \tag{6.39}$$

If v is big then:

$$\frac{\overline{x_w}}{\overline{x_n}} \cong 1 + \frac{1}{\nu} \cong 1 \tag{6.40}$$

1. **Vicat softening temperature**: is the temperature that, during heating at a constant and predetermined rate, a flat tip needle with an area of 1 mm^2 (1.120 mm $< D <$ 1.137 mm), penetrates the sample at a depth of 1 ± 0.01 mm, subject to a constant and predetermined load. Two types of loads, 10 ± 0.2 N (1 kg = 9.80665 N) or 50 ± 1.0 N, are used and heating rates of 50 ± 5 °C/h or 120 ± 10 °C/h. ASTM 1525 standardizes this method.
2. **Heat distortion temperature, HDT**: is the temperature that, during heating at a constant rate of 2 ± 0.2 °C/min, a rectangular section bar of 13 mm thickness and length between supports of 100 mm, positioned in its side and tensioned in the center, deforms the bar 0.25 mm (0.01 in). The maximum fiber tension (S) should be 0.455 MPa (66 psi) or 1.82 MPa (264 psi). ASTM 648 standardizes this method.

7.6 Effect of the Chemical Structure on T_g and T_m

Since the T_g and T_m transition temperatures refer to overcoming secondary forces and giving mobility to the polymer chain, any factor leading to an increase in secondary intermolecular forces and chain stiffness will increase both T_g and T_m. Figure 7.7 shows the positioning in the space T_m vs T_g, with values presented in degrees Celsius, of a long list of semi-crystalline polymers. The maximum range of the T_g is $-100\ °C \le T_g \le 300\ °C$ and for the T_m is $0\ °C \le T_m \le 400\ °C$, making a total span of 400 °C in both cases. These ranges are extremely convenient because they provide polymers for many types of commercial applications with varying levels of thermal stability. For example, applications where the material is expected to perform exclusively at room temperature and do not require any high mechanical strength can be provided by polyolefin, whose range is $100\ °C \le T_m \le 200\ °C$, which is considered a low melting temperature range. On the other hand, applications where the materials will have to perform at constant temperatures in the range of 100 °C should have a range of $200\ °C \le T_m \le 300\ °C$, which is considered a medium-high melting temperature, requiring the use of engineering thermoplastics.

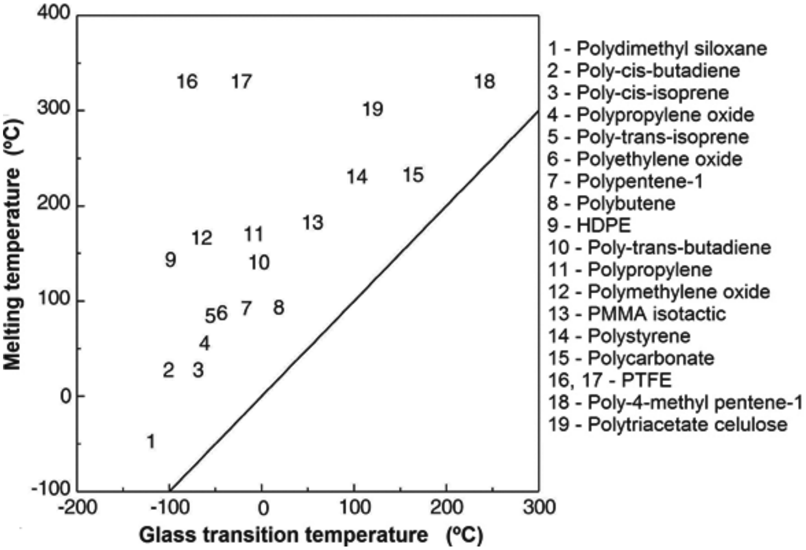


Figure 7.7 Relationship between the T_m and T_g values of various commercial polymers. The line represents $T_m = T_g$

The large variation in the values of T_g and T_m presented by the polymers is dependent on particular structural factors. The most important are listed, commented on, and exemplified in the next section. It is also possible in some cases to change them further by making use of external factors, which will be discussed in the next section of this chapter.

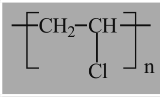
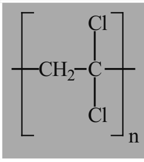
7.6.1 Structural Symmetry of the Main Chain

In Figure 7.7, it can be seen that most of the polymers present a difference between the transition temperatures of the order of 110 °C. On the other hand, some polymers present a greater difference. According to the **Boyer/Beaman Law**, the greater the symmetry of the polymer chain with respect to its side groups, the greater the difference between T_g and T_m. Taking the temperature in Kelvin, one gets:

1. $\frac{T_g}{T_m} \cong 0.5$ for **symmetrical polymers** either without a lateral group, as in PE, POM, etc., or with two groups symmetrically placed on both sides of the same carbon atom, as for PTFE, PVDC, etc.
2. $\frac{T_g}{T_m} \cong 0.75$ for **asymmetrical polymers** either with only one side group, as for PP, PS, PVC, etc., or two that should be very different in size, as in the case of PMMA.

The presence of side groups may not increase T_g and T_m at the same level when they are arranged symmetrically with respect to the main chain axis. This allows for better-balanced motions of the molecule, not requiring high levels of energy to achieve mobility. This effect is confirmed by the values of the transition temperatures of polyvinylidene chloride, PVDC, which are lower than those of polyvinyl chloride, PVC, although the former presents twice as many chlorine atoms as the PVC (and therefore a lateral group with double the volume) but they are disposed symmetrically, with a chlorine atom on each side of the polymer chain, as seen in Table 7.1.

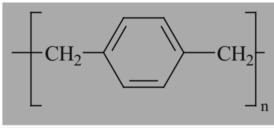
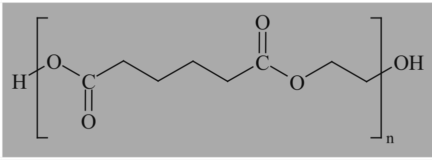
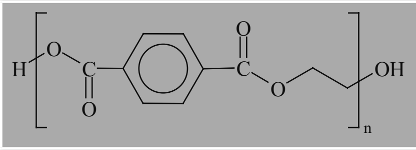
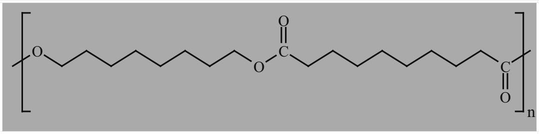
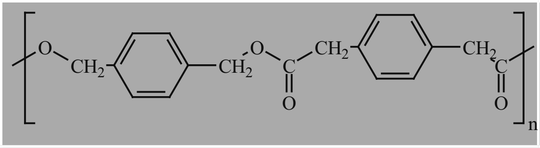
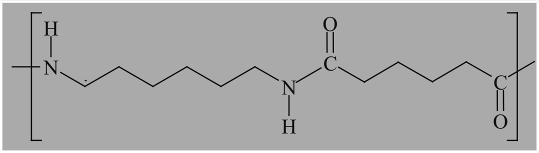
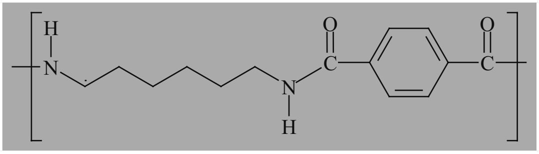
Table 7.1 T_g and T_m of Some Vinyl Polymers

Polymer	Mer	T_g (°C)	T_m (°C)	T_g/T_m (K/K)
Polyvinyl chloride PVC	 $-[CH_2-CH(Cl)]_n-$	87	212	0.74
Polyvinylidene chloride PVDC	 $-[CH_2-CCl_2]_n-$	-19	198	0.54

7.6.2 Rigidity/Flexibility of the Main Chain

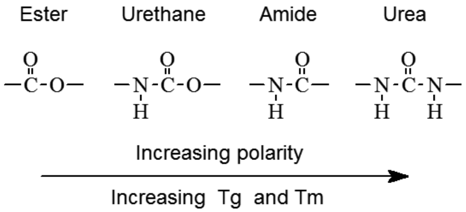
The presence of rigid groups within the main chain will promote rigidity, leading to an increase in both T_g and T_m. An example is the ***p*-phenylene rigid group** with two single bonds flat within the plane defined by the benzene ring. This is found in PET with T_g = 69 °C and T_m = 265 °C. In contrast, another polymer with a similar chemical structure, but not containing the *p*-phenylene group, polyethylene adipate (PEA), has much lower values (T_g = –46 °C and T_m = 45 °C); it, therefore, has fewer commercial applications. The same happens with other polymers (polyamides, polyesters, etc.) where ethylene sequences are replaced by *p*-phenylene groups. On the other hand, some elements can generate chain flexibility as in the case of **oxygen** and **sulfur** atoms because they form flexible bonds with carbon. Thus, polyethylene oxide, which has a flexible ether bond –C–O–C– within the main chain, has a T_m = 66 °C, much lower than the value given by polyethylene, which is T_m = 135 °C. For a comparative analysis between various chemical structures, analyze the examples presented in Table 7.2.

Table 7.2 Stiffening Effect of the *p*-Phenylene Group on Some Condensation Polymers

Polymer	Mer	T_g (°C)	T_m (°C)
Polyethylene (PE)	$\left[CH_2\text{-}CH_2 \right]_n$	–100	135
Polyethylene *p*-phenylene			380
Polyethylene oxide	$\left[CH_2\text{-}CH_2\text{-}O \right]_n$		66
Polyethylene adipate (PEA)		–46	45
Polyethylene terephthalate (PET)		69	265
Polyoctene sebacate			75
Aromatic polyester			146
Polyhexamethylene adipamide (nylon 6,6)		87	263
Polyhexamethylene terephthalamide (nylon 6T)			350

7.6.3 Polarity of the Main Chain

The existence of polar groups in polymer macromolecules causes a strong attraction between the chains, bringing them closer together and increasing the secondary forces. Thus, the presence of **polarity** increases T_g and T_m, and they are greater the higher the polarity value. Common polar groups in polymers include the carbonyl group, $-\overset{O}{\overset{\|}{C}}-$, in which its polarity value will be affected depending on the type of atom bonded laterally to it. Nitrogen atoms tend to donate and oxygen to withdraw electrons, respectively. Ester, urethane, amide, and urea polar groups have increasing polarity in this order and therefore polymers with similar chemical structures (changing only the polar group but keeping their content along the polymer chain constant) increase T_g and T_m in this order.



$$-\overset{O}{\overset{\|}{C}}-O- \quad -\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O- \quad -\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}- \quad -\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-$$

This effect can also be seen in Figure 7.8 where the change of the melting temperature of several homologous series (with the same functional group) of aliphatic polymers (with linear CH_2-methylene sequences) is shown as a function of the number of CH_2 groups connecting the functional groups. For the same number of methylenes, the higher the polarity of the functional group present, the greater the T_m of the polymer. On the other hand, the higher the number of CH_2s, the lower the concentration of the functional groups per unit length of molecule and, therefore, the lower its attraction effect. In this way, the values of T_m are close to that presented by a very long sequence of methylenes, which is no more than polyethylene itself. Table 7.3 exemplifies the latter case for a series of linear aliphatic polyamides. When the number of methylenes is even, both N–H and C=O bonds are placed at the same side of the main chain; when it is odd, they sit on opposite sides. This particular configuration affects the crystallization kinetics and the melting temperature.

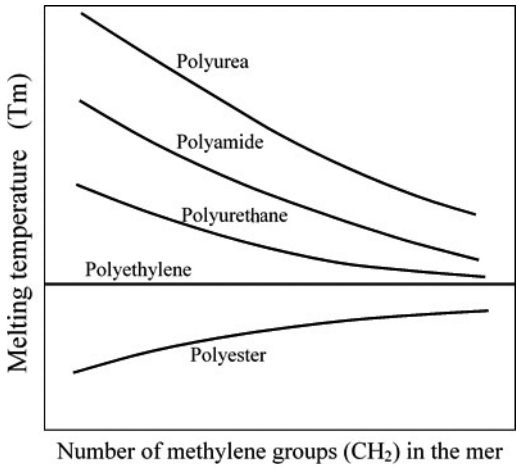
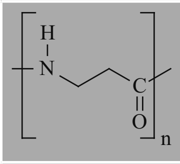
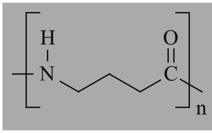
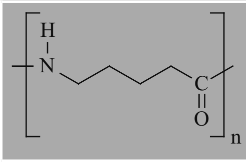
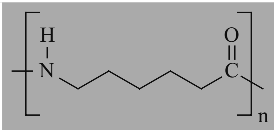
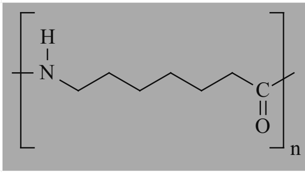


Figure 7.8 Variation of T_m for several homologous series of aliphatic polymers

Table 7.3 Melting Temperatures of Some Polyamides (Nylon N)

Nylon type	Mer of some nylon types	T_m (°C)
3		320–330
4		260–265
5		260
6	 Polycaproamide	215–220
7		225–230

2. Discuss how copolymerization and chain branching affect the radius of interaction *R*. What experimental technique makes use of this property to characterize different types of homopolymers and copolymers?
3. Justify why Eq. (10.2) (from Chapter 3, Section 3.5.4) is valid. What is the advantage of it being valid for the commercial production of a thinner?

$$\delta^{\mathrm{m}} = \sqrt{\left(\delta_{\mathrm{d}}^{\mathrm{m}}\right)^2 + \left(\delta_{\mathrm{h}}^{\mathrm{m}}\right)^2 + \left(\delta_{\mathrm{p}}^{\mathrm{m}}\right)^2} \tag{10.2}$$

■ 10.4 Identification of Polymers by Infrared Absorption Spectroscopy

10.4.1 Objective

Use the infrared absorption spectroscopy FTIR technique for a qualitative analysis in the identification of the chemical structure, molecular configuration, components, formulation, etc., of pure polymers, their blends, and composites.

10.4.2 Introduction

Infrared absorption spectroscopy is one of the most widely used tools for identifying and characterizing polymeric materials. The vibrational analysis of polymers can provide information on three important structural aspects: chemical composition, configurational, and conformational structure. It also provides indications of interatomic forces due to the presence of molecular interactions. The technique of characterization of materials by absorption in the infrared is based on the observation of the frequency (qualitative analysis identifying the type of chemical bond) and intensity (quantitative analysis measuring the chemical bond concentration) of absorbed infrared radiation when a beam of this radiation crosses the sample. The infrared region corresponds to the range of wavelengths of the electromagnetic spectrum of 1 micron to 1 mm.

For a molecule to absorb infrared radiation, a change in the dipole moment of the molecule must occur during its axial and angular deformation movements. The incidence of infrared radiation in the molecule at the same frequency as the vibration of one of its bonds absorbs part of the incident energy with increasing amplitude of this vibration. By measuring the decreases in intensity of the transmitted radiation, a spectrum of the absorbed infrared radiation, characteristic of the material being analyzed, is generated.

The atoms that make up a molecule are in continuous motion due to various types of vibrations. They can be classified into two fundamental modes: **axial deformation** (or stretch) and **angular deformation**, shown in Figure 10.2 for a triatomic molecule. These vibrations occur only on some quantized frequencies, that is, they are unique and characteristic of each chemical bond.

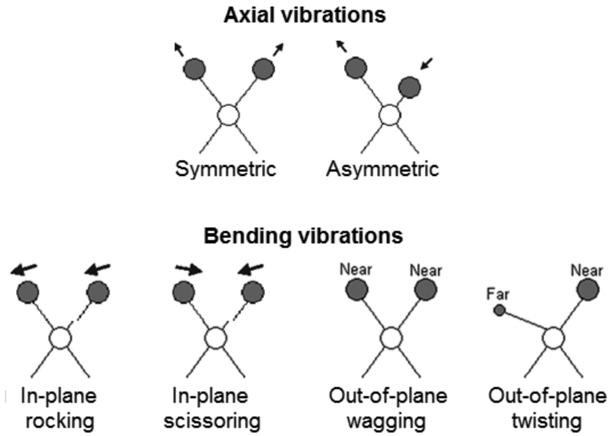


Figure 10.2 Vibration modes of a simple three-atomic molecule

If a radiant energy of known intensity at all wavelengths of its spectrum is supplied to the sample through an incident beam and the intensities at each particular wavenumber of the transmitted beam are analyzed, it may be seen that the intensity will be lower with some particular wavenumbers. This means that chemical bonds present in the sample selectively absorb at these frequencies. Such knowledge allows the identification of some of the bonds present in the sample contributing to their identification. In practical terms, spectra of the unknown sample can be compared with standard sample spectra facilitating the identification of the material. Figure 10.3 shows the infrared absorption spectrum of polystyrene.

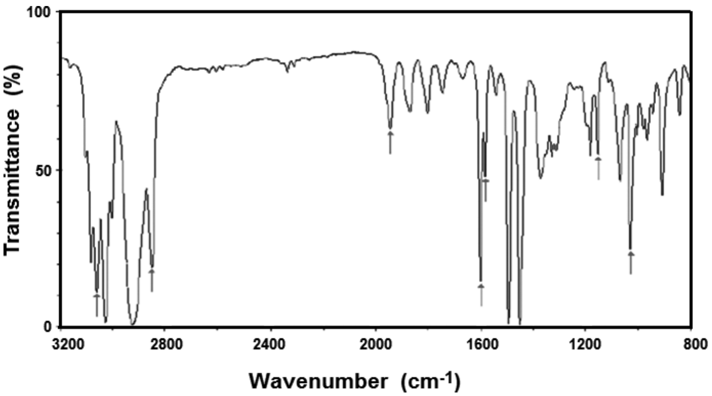


Figure 10.3 Infrared absorption spectrum of a polystyrene PS thin film. The arrows indicate some of the bands used to calibrate the equipment

A large number of polystyrene characteristic bands can be used for spectrophotometer calibration. Table 10.4 shows these reference bands, some with precision to the first decimal place (in cm^{-1}). The table also gives an indication of the relative intensity of each band, assuming the strongest ones have a maximum intensity of 10.

Table 10.4 Wavenumber for Some Absorption Bands Characteristic of Polystyrene and Their Relative Intensity, Normalized between Zero (baseline) to 10 (Highest Absorption)

Wavenumber (cm^{-1})	Relative intensity	Wavenumber (cm^{-1})	Relative intensity	Wavenumber (cm^{-1})	Relative intensity
3027.1	9	1583.1	5	1154.3	4
2924	10	1495	10	1069.1	6
2850.7	7	1454	10	1028.0	8
1944.0	3	1353	5	906.7	3
1871.0	3	1332	5	842	3
1801.6	3	1282	3	752	10
1601.4	9	1181.4	4	698.9	10

The identification of an unknown sample is done by analyzing the position and intensity of the absorption bands present in the spectrum, comparing them with standard tables. In this experiment, it is initially suggested to try the identification of pure and known polymers. After the operator has acquired some experience, it is recommended that they identify polymer plastic products found on the market such as packaging, pipes, pots, films, injected parts, etc.

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