

CHAPTER III

CHARACTERIZATION

3.1 Molecular weight and molecular weight distributions

While the exact molecular weight required for a substance to be called a polymer is a subject of continued debate, often polymer scientists put the number at about 25,000 g/mol. This is the minimum molecular weight required for good physical and mechanical properties for many important polymers. This molecular weight is also near the onset of entanglement.

3.1.1 Molecular weight average

The same polymer from different sources may have different molecular weights. Thus polyethylene from source A may have a molecular weight of 150,000 g/mol, whereas polyethylene from source B may have a molecular weight of 400,000 g/mol (Figure 3.1). To overcome this difficulty, the molecular weight distribution is thus employed since all synthetic polymers and most natural polymers (except proteins) have a distribution in molecular weights. The differences result directly from the kinetics of polymerization (Cambell and While, 1985).

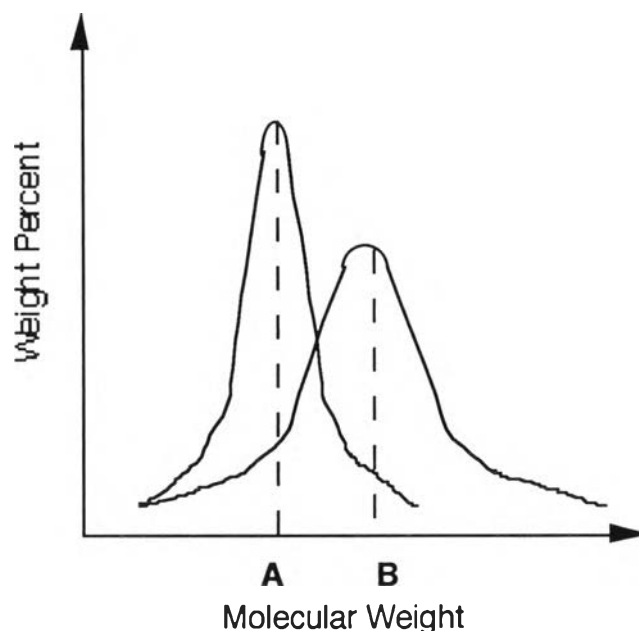


Figure 3.1 Molecular weight distribution of the same polymer from two different sources, A and B.

However, these facts led to much confusion for chemists early in the 20th century. At that time, chemists were able to understand and characterize small molecules, such as hexane having six carbon atoms. If polyethylene with 2430 carbon atoms were declared to be “polyethylene”, how could that component having 5280 carbon atoms also be polyethylene? How could two sources of the material having different average molecular weights both be polyethylene?

The answer to these questions lies in defining average molecular weights and molecular weight distributions. The two most widely used molecular weight averages are the number-average molecular weight, M_n , and the weight average molecular weight, M_w ,

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

where N_i is the number of molecules of molecular weight M_i .

For single-peaked distributions, M_n is usually near the peak. The weight-average molecular weight is always larger. For simple distributions, M_w may be 1.5-2.0 times M_n . The ratio M_w/M_n , sometimes called polydispersity index, provides a simple definition of the molecular weight distribution. Thus all compositions of $(-\text{CH}_2-\text{CH}_2-)_n$ are called polyethylene, whose the molecular weights are specified for each specimen.

For many polymers, a narrower molecular weight distribution yields better properties. The low end of the distribution may act as a plasticizer, softening the material. Certainly it does not contribute as much to the tensile strength. The high-molecular-weight tail increases processing difficulties, because of its enormous contribution to the melt viscosity. For these reasons, great emphasis is placed on characterizing polymer molecular weights.

3.1.2 Gel permeation chromatography

Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) has developed into one of the most useful methods for routine determination of average molecular weights and molecular weight

distributions of polymers. It is the facility which makes the technique so attractive to polymer scientists and technologists allied to the development of on-line microprocessor based data handling which facilitates the calculation of the molecular weight averages from the size distribution chromatograms. In addition, only very small sample sizes are required permitting, for example, studies of the effects of weathering on the surface of polymers.

GPC is a form of liquid chromatography in which the molecules are separated according to their molecular size. The procedure involves injecting a dilute solution of a polydisperse polymer into a continuous flow of solvent passing through a column containing tightly packed microporous gel particles. The gel has particle sizes in the range of 5-10 μm in order to give efficient packing and typically possesses a range of pore sizes from 0.5 to 10⁵ nm, which correspond to the effective size range of polymer molecules. Separation of the molecules occurs by preferential penetration of the different sized molecules into the pores: small molecules are able to permeate more easily through the pores, as compared to the larger sized molecules so that their rate of passage through the column is correspondingly slower. The continuous flow of solvent leads to separation of the molecules according to size, with the larger molecules being eluted first and the smaller molecules, which have penetrated more deeply into the pores, requiring longer elution times. Consequently, selection of the column packing material to have the appropriate pore size distribution is crucial and different columns are usually required for polymer having widely different molecular weight distributions. The recent availability of gels of mixed pore sizes which can operate over four decades of molecular weight has made this a less demanding requirement (Campbell and While, 1989).

3.2 Isotacticity

The method based on IR measurement have proved the most widely used in determination of polypropylene isotacticity. This is probably a consequence of the ready availability of the instrumentation, ease, and simplicity of sample preparation and measurement.

Whereas, the IR spectrum of isotactic polypropylene was first reported by Natta and co-workers, the first quantitative study seeking to relate isotacticity with IR adsorption intensity was published by Luongo. The results of this are still widely quoted today. Loungo showed that the ratio of absorbances at 995 and 970 cm^{-1} was a function of the isotacticity of the sample. The absorption band at 995 cm^{-1} is due to isotactic helices, as shown in figure 3.2 . The band at 970 cm^{-1} is independent of isotacticity and has been used as a reference band (Kissin,1975).

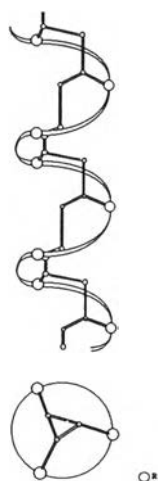


Figure 3.2 Helical conformation of isotactic polypropylene.

Loungo established a calibration curve relating the absorbance ratio to isotactic content by using physical mixtures of supposed completely isotactic and atactic materials, as shown in figure 3.3 (Burfield and Loi, 1992).

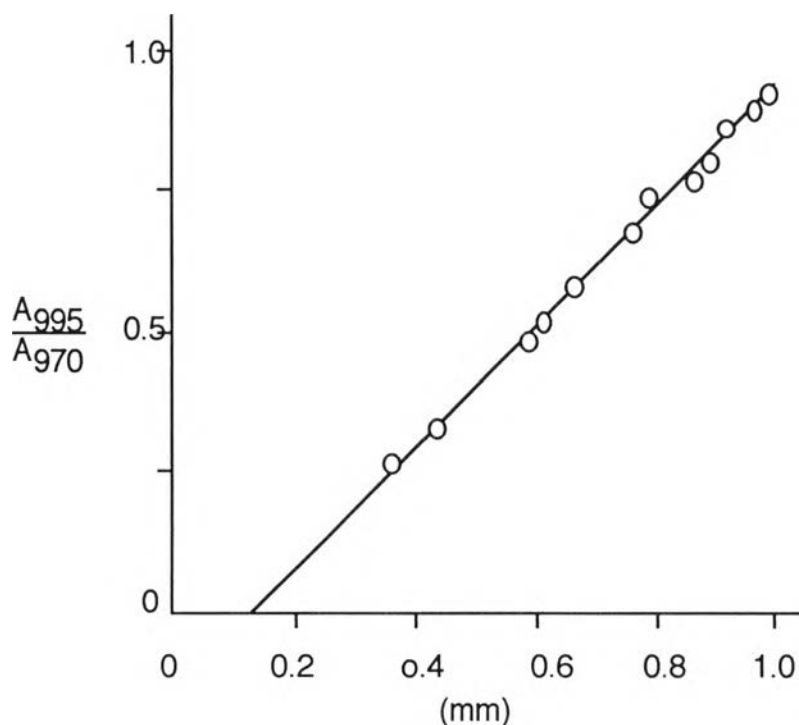


Figure 3.3 Calibration curve for IR absorbance ratio A_{995}/A_{970} .
(mm) = Isotactic Index

3.3 Degree of crystallinity

One of the most important characteristics of a given sample of a polymer is its degree of crystallinity, defined as the weight fraction of crystalline material in the sample. The definition is only apparently simple, because various types of more or less ordered structures have been recognized and may coexist in a polymer. It may turn out to be very difficult

to classify some of these structures as crystalline and others as amorphous (Kampf, 1986).

The X-ray diffraction pattern is intermediate in character between that given by a crystalline and that given by an amorphous polymer, as shown in figure 3.4.

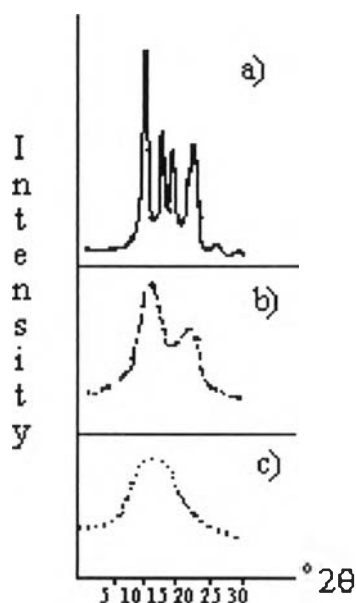


Figure 3.4 Comparison between the X-ray Geiger spectra ($\text{CuK}\alpha$) of
 (a) crystalline isotactic polypropylene
 (b) paracrystalline isotactic polypropylene
 (c) amorphous atactic polypropylene

It has been possible to distinguish in the X-ray spectrum of a polymer between the X-ray intensity diffracted from amorphous regions and that diffracted from the crystalline regions. This is the basis of the most popular

method of crystallinity determination. This method relies upon the assumption that the weight fraction of crystalline polymer is proportional to the energy diffracted from crystalline regions, whereas the weight fraction of amorphous polymer is proportional to the energy diffracted from amorphous regions. The degree of crystallinity is calculated from a comparison of the diffracted energies.

3.4 Melting point

The significance of *thermoanalytic* methods lie not only in the fact that the thermal properties of polymer are important for producers and users but also that the technological properties of plastics depend on their thermal history to a great extent.

One of the important *thermoanalytic methods* is differential scanning calorimetry (DSC). The procedure permits the amount of heat taken up from or given off to the surrounding per unit time during isothermal procedure or during heating or cooling to be measured precisely.

The peak areas from DSC are always proportional to the amount of energy taken up by or given off from the sample, as shown in figure 3.5. From DSC diagram, melting point of a polymer are determined and in case of crystalline polymers the crystalline fraction can also be determined by calibration with reference samples.

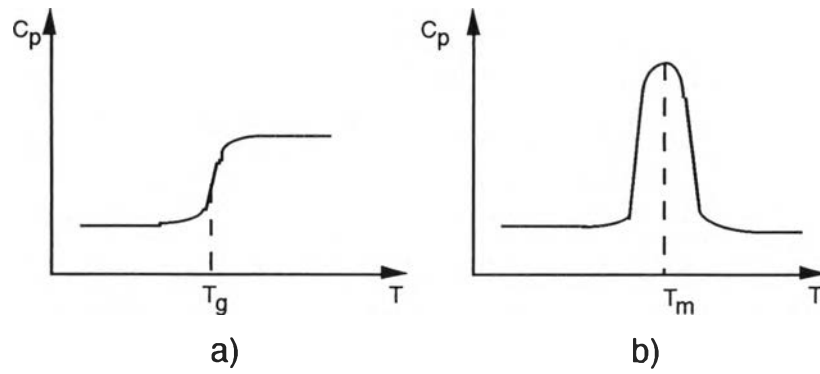


Figure 3.5 Typical DSC diagram for

a) Amorphous polymers : T_g = Glass transition temperature

b) Crystalline polymers : T_m = Melting point

C_p = Specific heat.