17

POLYMER MOLECULAR WEIGHT MEASUREMENT

María Guadalupe Neira-Velázquez, María Teresa Rodríguez-Hernández, Ernesto Hernández-Hernández, and Antelmo R. Y. Ruiz-Martínez

17.1 INTRODUCTION

Gel permeation chromatography (GPC), also known as *size-exclusion chromatography* (*SEC*), is a chromatographic technique that employs specialized columns to separate natural and synthetic polymers, biopolymers, or proteins on the basis of their size. GPC is the most widely used technique for the analysis of polymers, in relation to other techniques of molecular weight (MW) measurement; the analysis is very fast (compared to older techniques) and can be carried out in a couple of hours. It can be used for samples soluble in organic and aqueous eluents, and for MWs from approximately 100 to several million daltons (Da). With GPC, it is also possible to obtain the MW of polymers that are soluble only at high temperatures. Besides, in contrast to traditional techniques, it yields all MW averages and the molecular weight distribution (MWD).

17.2 HISTORICAL BACKGROUND

The word chromatography was used for the first time in 1906 by a Russian botanist, Mikhail Tswett, who described it as a new technique to separate the components of complex mixtures [1, 2]. His work was published in the Proceedings of the German Botanical Society; there he described a technique based on the partition of solutes between a stationary solid adsorbent and a moving liquid phase. The experiment consisted in pouring a small quantity of the solution of pigments, such as green leaf pigments, on the top of a vertical column of absorbent, followed by a flow of pure solvent, whereupon a series of colored bands formed down the length of the column in a sequence determined by mass relationships and absorption coefficients [3].

Despite the tremendous potential impact of his discovery, chromatography was not revived until 1931, under the stimulus of widespread research on the separation of carotenoids from several natural sources by adsorption analysis on fibrous alumina [4]. Since the cited work was published, chromatography application has been extended over practically all areas of chemistry. In polymer science, chromatography was used for the first time by Moore in 1963 to determine the MWD of polymers [5].

The technique was really invented by Lathe and Ruthven [6], who were working at Queen Charlotte's Hospital in London. They received the John Scott Award for their invention. In 1964 Moore, from the Dow Chemical Company, prepared GPC columns using crosslinked polystyrene with controlled pore size [7]; after publishing his results, there was a rapid increase of research activity in the field of measurement of the MW of polymers.

James Waters, industry pioneer and entrepreneur, had founded Waters Associates (WA) in 1958 in order to invent instruments for others. He worked with five employees in the rented basement of a police station. In 1961 John Moore required from WA to develop a 0.1 ml volume flow cell, which would enable him to develop an instrument using gel columns to analyze the MW of polymers (natural and synthetic macromolecules). After experimental work by Moore, followed by negotiations between Dow and WA and additional hard work to scale up the synthesis of the polymeric gel used in the columns, the invention of the GPC was completed, becoming a major breakthrough for WA.

Handbook of Polymer Synthesis, Characterization, and Processing, First Edition. Edited by Enrique Saldívar-Guerra and Eduardo Vivaldo-Lima.

In 1963, Waters obtained an exclusive license to Dow's patent [5] for GPC and introduced Waters' first liquid chromatography (LC) system, the GPC 100, which was larger than a refrigerator.

17.3 PRINCIPLES OF GPC

17.3.1 Principle of Separation

The fundamental principle of separation by size exclusion in a column is represented in Figure 17.1. The column is packed with semisolid particles of a polymer whose structure is crosslinked to form a gel and whose pore distribution has been controlled during the synthesis of the polymer. Molecules that are smaller than the pore size can enter inside the pores and therefore have a longer path and a longer transit time than larger molecules which cannot enter the pores. Molecules larger than the pore size cannot enter the pores and elute before smaller molecules. This condition is called *total exclusion* because of the fact that the largest molecules are rejected from entering the pores, as shown in Figure 17.1. Molecules that can enter the pores will have an average residence time in the particles that depends on the molecular size and shape.

The separation parameters in GPC are obtained by the distribution coefficient k_d, related to the internal volume according to

$$k_d = \frac{V_{i,acc}}{V_i} = \frac{V_e - V_0}{V_0} \tag{17.1}$$

where $V_{i,acc}$ is the accessible internal volume, V_i is the internal volume, V_e is the elution volume, and V_0 is the external volume or interparticle volume. When $k_d = 0$, it means that the molecules are excluded; $0 < k_d < 1$ indicates that the molecules are retained in the gel pores; $k_d = 1$ suggests that the molecules occupy the total inner volume [8].

The fundamental principle of separation by SEC was described by Benoit and coworkers in 1967. They found an excellent correlation between the elution volume and a dynamically based molecular size, the hydrodynamic volume V_H[1] for a wide range of species and large-scale molecular architectures [9]. Their theory assumed a thermodynamic separation principle considering that the elution volume is independent of the flow rates. Recently, it has been proved that the radius of gyration is more appropriate than the hydrodynamic volume [10]. The radius of gyration R_g is defined as the mean square distance away from the center of gravity [11]. Its mathematical definition is:

$$R_g^2 = \left(\frac{1}{N}\right)\sum_{i=1}^{N} r_i^2 \tag{17.2}$$

[1]The hydrodynamic volume is proportional to the product of the molecular weight M and the intrinsic viscosity $[\eta]$; that is, $V_H \propto [\eta]M$.

which is the radius of gyration of N scattering points located at distances r_i. In mechanical terms, R_g can be interpreted as the radius of a thin ring that has the same mass and same moment of inertia as the body when this is centered around the same axis [12]. Furthermore, calculations indicate that the morphology of polymers in solution is not spherical in overall shape, but rather ellipsoidal [13]. In terms of their overall shape, branched polymers are more symmetric than linear ones [14]. This explains some of the differences between linear and branched polymers with respect to size exclusion. Similar arguments have been used to explain the failure of R_g to provide an appropriate size measure for the SEC of oligomers of polyethylene and polystyrene [15, 16].

GPC is the technique of choice for rapid and reliable characterization [17] of MW averages, MWD, and molecular structure for all types of macromolecules—proteins, oligomers, natural polymers, and synthetic polymers.

The polymer characteristics that can be measured by GPC can be listed as

- absolute MW;
- MWD;
- MW averages (see below) and dispersity of the MWD (formerly called *polydispersity*);
- branching and structure;
- molecular size;
- copolymer composition.

17.3.2 Average Molecular Weight of Polymers

The following MW averages can be obtained by GPC:

$\overline{M_n}$, number-average MW;
$\overline{M_p}$, peak-average MW;
$\overline{M_v}$, viscosity-average MW;
$\overline{M_w}$, weight-average MW;
$\overline{M_z}$, Z-average MW;
$\overline{M_{z+1}}$, $Z+1$-average MW.

The different MW averages can also be measured by the techniques shown in Table 17.1. The main disadvantage of other techniques to measure average MW in polymers is that they are very time consuming. In some cases, just one of these MWs is obtained in a week. On the other hand, by using GPC the different averages of MW can be obtained in about 2 h.

The MW averages $\overline{M_n}$, $\overline{M_w}$, $\overline{M_z}$, $\overline{M_{z+1}}$, and $\overline{M_v}$, are mathematically defined in Section 1.5 of Chapter 1. For any MWD, the various average MWs always rank in the order $\overline{M_n} < \overline{M_v} < \overline{M_w} < \overline{M_z} < \overline{M_{z+1}}$. If all the average MWs are the same, then we have a monodisperse polymer.

$\overline{M_n}$ and $\overline{M_w}$ are the most commonly used average MWs; in industry, it is usually enough (although not always) to

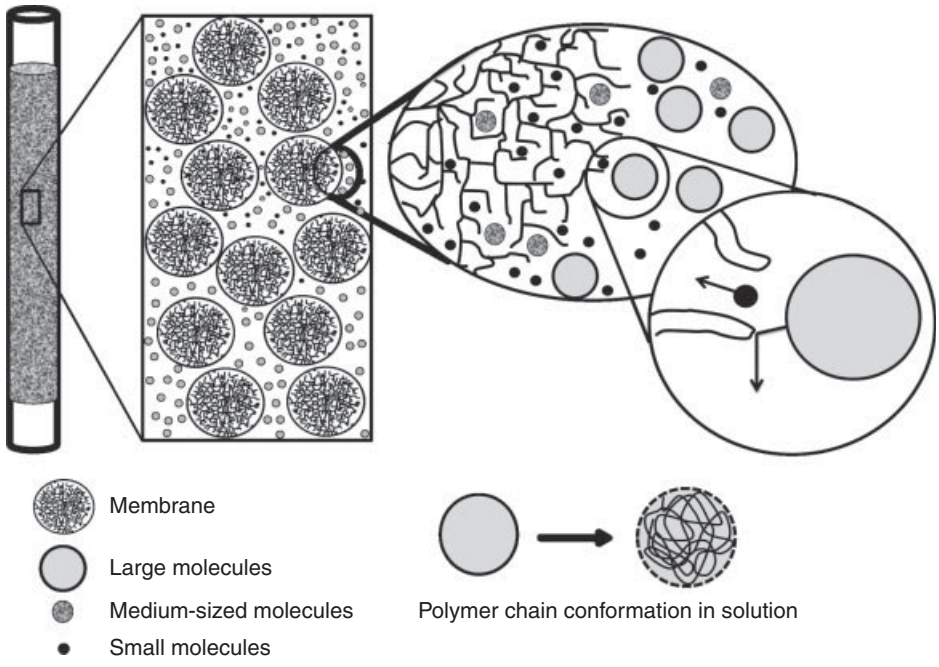

Figure 17.1 Illustration of the separation of polymer molecules by size exclusion.

TABLE 17.1 Techniques for Measuring Different Molecular Weight Averages

Average Molecular Weight	Technique
$\overline{M}_n$	Vapor pressure osmometry
	End-group titration
	Proton NMR
	Boiling point elevation
	Freezing depression (cryoscopy)
	GPC
$\overline{M}_w$	Light scattering
	Small-angle neutron scattering (SANS)
	X-ray scattering
	Sedimentation velocity
	GPC
$\overline{M}_v$	Viscometry
	GPC
$\overline{M}_z$	Ultracentrifugation
	GPC
$\overline{M}_{z+1}$	Ultracentrifugation
	GPC

know them to describe the main features of the MWD of a polymer.

Osmotic pressure and vapor pressure methods are used to determine absolute values of $\overline{M}_n$, while light scattering and sedimentation velocity are used to determine $\overline{M}_w$. However, if the GPC equipment is coupled with different detection techniques, such as light scattering, viscometry, refractive index, etc., then it is possible to obtain absolute MWs of polymers. Table 17.1 shows the different techniques used to measure different average MWs of polymers. It can be appreciated that GPC measures all MW averages. The different average MWs obtained by GPC can be represented in a MWD curve, as appreciated in Figure 17.2.

The MW dispersity had been already defined in Section 1.5 of Chapter 1, and is the ratio $\overline{M}_w/\overline{M}_n$. Polymers with a narrow distribution (low MW dispersity) are more suitable for injection molding, whereas polymers with

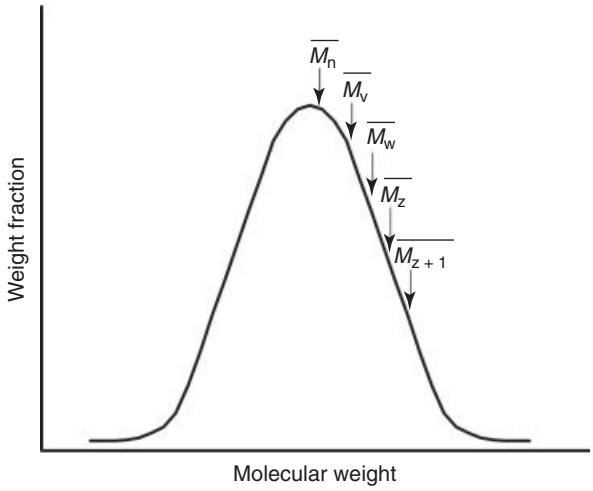

Figure 17.2 Schematic plot of a distribution of MWs showing the different averages of MW.

TABLE 17.2 Various Average Molecular Weights and their Relation with Polymer Properties

Molecular Weight	Polymer Properties
Number-average molecular weight ($\overline{M}_n$)	Tensile strength, impact strength, and hardness
Weight-average molecular weight ($\overline{M}_w$)	Brittleness
Z-average molecular weight ($\overline{M}_z$)	Deflection and rigidity

a high MW dispersity are more suitable for extrusion. Polymers with a MW dispersity of 1.0 can be produced only by biological systems. Many physical properties can be affected by the MW dispersity.

The physical and chemical properties of the polymers in general are directly related to the MW, MWD, MW dispersity, and long-chain branching [18, 19]. Table 17.2 shows the relationship between the average MWs and some physical properties of polymers. There is also a relationship between the MW and the viscoelastic properties of polymers [20, 21] and thus it is possible to predict some properties of the polymer with a simple determination of the MW by GPC. Polymers with high MWs have higher viscosity, they also present low melt flow index, and are more difficult to dissolve, since they present higher chemical resistance; polymers with very high MW are more difficult to process and require higher temperatures.

17.3.3 GPC Systems

A GPC system consists of various instruments. Injectors are used to introduce the polymer solution into the columns of separation. Pumps deliver the sample and solvent through the columns and the system. Detectors record the exit of fractions of the sample and count the number of molecules of a certain MW. The computer controls the test automatically, records the results, and calculates the different MW averages. The GPC system contains a number of different instruments that work together to provide the optimum system performance. Figure 17.3 shows a schematic of a gel permeation chromatograph with the basic components.

17.3.3.1 Injector The injector introduces the polymer solution into the mobile phase. It must be capable of injections of small and large volumes. It should not interfere with the continuous mobile phase flow. It should be capable of multiple sample injection and should be capable of self-cleaning between injections. In the past, the injections were carried out manually, but this is not the case at present, since most of the GPC instruments have automatic injectors.

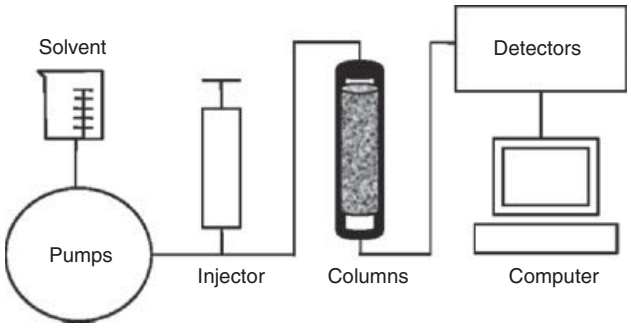

Figure 17.3 Schematic representation of the components of a GPC system.

17.3.3.2 Pumps These are piston-type precision pumps. They pump the polymer in solution through the system. The pump must deliver the same flow rates throughout the time in order to maintain the same pressure inside the system. Any variation in flow rates affects directly the results. The pump also has to deliver the same flow rates independently of the viscosity differences. In addition, some detectors are highly sensitive to the solvent flow rate precision. Such constant flow is a critical feature of the instrument.

17.3.3.3 Columns They are considered the heart of the equipment. The separation of the macromolecules takes place in their interior. They are filled with a porous crosslinked polymer, and the macromolecules to be separated interact with the polymer pores depending on their size in solution. It is highly recommended to use at least a set of three columns in order to obtain good results. Columns are available at different pore sizes. Columns with very small pores sizes are used for polymers of low MW, while columns packed with material containing large pore sizes are used for polymers with high MW. High efficiency columns give maximum separating capability and rapid analyses. Every column must provide reproducible information over extended periods for both analytical and fraction-collection purposes. There are columns for different types of applications. For example, there are columns that can stand high temperatures, which are used to fractionate polymers that are soluble only at high temperatures, such as polyethylene or polypropylene. There are also columns suitable to work with aqueous solvents, those columns are packed with a material known as *ultrahydrogel*, which is basically a crosslinked hydroxylated polymethacrylate; these columns are used with polymers that are soluble in water, such as poly(acrylic acid), poly(vinyl alcohol), poly(ethylene glycol), etc.

17.3.3.4 Detectors The detectors used in a GPC system monitor the separation and respond to the components and/or fractions as they elute from the column.

Detectors must be sensitive and must have a wide linear range in order to respond to both trace amounts and large quantities of material, if necessary. They must be nondestructive to the eluting components if they are to be collected for further analysis. There are different types of detectors for GPC, the most common ones being the refractive index (RI) detector, the UV detector, viscometer detector, as well as light scattering and infrared detectors.

Since all compounds refract light, the RI is known as a "universal" detector. It is the most widely used detector to monitor the MWD. The refractive index of polymers is constant above approximately 1000 Da. Therefore, the detector response is directly proportional to the concentration.

In addition to the information about MW averages and distribution obtained with the RI detector, UV absorbance detectors may provide information about composition. UV detectors are used for polymers containing chromophore groups.

Online light scattering detectors and viscometers provide information about the polymer structure. If a light scattering detector is used together with an RI, then it is not necessary the use of polymer standards to calibrate the equipment, since light scattering gives the absolute weight-average MW ($\overline{M_w}$). Light scattering detectors also measure the radius of gyration. Viscometer detectors also provide information about the intrinsic viscosity of the polymer and the level of branching (index of branching) of the polymeric chains. The more the number of detectors coupled to the GPC equipment, the more detailed is the structural and chemical information of a polymer that can be obtained.

17.3.3.5 Computer The computer automatically calculates, records, and report numerical values for $\overline{M_n}$, $\overline{M_w}$, $\overline{M_v}$, $\overline{M_z}$, $\overline{M_{z+1}}$, and the MWD. It can also provide complete control of GPC systems so that large numbers of samples can be run unattended and raw data can be automatically processed. Nowadays, the software used in GPC should be capable of providing special calculations for multidetection processing, special calibration routines, polymer branching, and intrinsic viscosity determination, etc.

SEC can be used as a measure of both the size and the MW dispersity of a polymer; that is, it has the capability of finding the distribution of the sizes of polymer molecules. If standards of a known size are run previously, then a calibration curve can be created to determine the sizes of polymer molecules of interest in the solvent chosen for analysis often tetrahydrofuran (THF). Alternatively, techniques such as light scattering and/or viscometry, which do not rely on the calibration using standards of known MW, can be used online with SEC to yield absolute MWs. Because of the difference in size of two different polymers with identical MWs, the absolute determination methods are, in general, more desirable.

17.3.3.6 Calibration In order to obtain the MW and the MWD of a polymer sample it is necessary to calibrate the equipment. To achieve this, solutions of some polymer standards of known MW and very narrow MWD are prepared by dissolving them in a suitable solvent; it is common to prepare the solution of polymer standards ("standards" for short) at a concentration of 0.1% (w/v). Two or more standards can be prepared in the same vial. In order to obtain a good calibration curve, it is recommended to run at least 10 polymer standards of MWs between 100 and 15,000,000 Da. Once the standards are injected into the GPC, the calibration curve is built plotting on the y-axis the log(MW) and on the x- axis the elution volume. The calibration curve has to be linear and is used by the equipment to obtain the different MWs of the unknown sample as well as the MWD (Fig. 17.4).

The following are the most popular narrow polymer standards for GPC: polystyrene, poly(methyl methacrylate), and poly(acrylonitrile). For samples soluble in water, the ones recommended are poly(acrylic acid), poly(ethylene glycol), poly(ethylene oxide), and poly(vinyl alcohol), among others.

17.3.3.7 Universal Calibration In the conventional calibration (described above), there is a problem when a sample that is chemically different from the standards used to calibrate the column is analyzed. However, this is a common situation; for instance, a polyethylene sample is run by GPC while the calibration curve is constructed with polystyrene standards. In this case, the MW obtained with the conventional calibration is a MW related to polystyrene, not to polyethylene. On the other hand, it is very expensive to construct calibration curves of every polymer that is analyzed by GPC. In order to solve this problem, a universal calibration technique, based on the concept of hydrodynamic volume, is used. As mentioned before, the basic principle behind GPC/SEC is that macromolecules are separated on the basis of their hydrodynamic radius or volume. Therefore, in the universal calibration a relationship is made between the hydrodynamic volume and the retention (or, more properly, elution volume) volume, instead of the relationship between MW and elution volume used in the conventional calibration. The universal calibration theory assumes that two different macromolecules will have the same elution volume if they have the same hydrodynamic volume when they are in the same solvent and at the same temperature. Using this principle and the constants K and α from the Mark-Houwink-Sakurada equation (Eq. 17.18), it is possible to obtain the absolute MW of an unknown polymer. The universal calibration principle works well with linear polymers; however, it is not applicable to branched polymers.

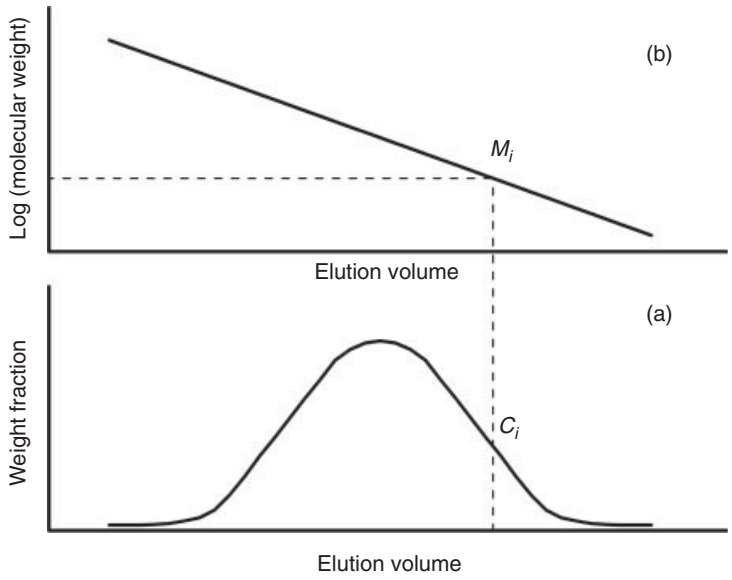

Figure 17.4 MW determination of (a) an unknown sample using (b) the calibration curve.

17.3.3.8 High Temperature Gel Permeation Chromatography (HT-GPC) HT-GPC measures the average MW and MWD of polymers requiring higher analysis temperatures.

Typically, GPC is performed at room temperature, using THF or chloroform as solvents, demanding simple separation hardware requirements. However, there are many polymers, some of high commercial importance, such as polyolefins, nylons, or polyesters, that exhibit limited solubility at room temperature because of their high crystallinity, and therefore, their MWs can be assessed only at high temperatures, making them soluble in certain solvents, such as toluene, xylene, and 1,2,4-trichlorobenzene [22, 23]. New parameters need to be introduced in HT-GPC including polymer configuration, retention volume, MW calibration errors, solvent, polymer degradation, and column efficiency as a function of separation temperature [22–26]. Nevertheless, it is accepted that HT-GPC has the advantages of reduced analysis time and increased separation efficiency. Polymers that cannot dissolve at room temperature, especially those with a high level of crystallinity, generally require the use of high temperature and stirring in order to destroy the crystals. On cooling, the polymer will recrystallize and precipitate from the solution. For this reason, high temperature is required throughout the entire analysis to ensure that the samples remain in solution during the experiment. Thus, it is necessary that the GPC system is equipped with a column heater in order to keep the polymer in solution and to obtain reliable and reproducible results. In general, all different sections of the equipment have to be kept at high temperature to avoid the precipitation of the polymer and the blockage of the tubing due to an increase of the pressure of the system. The equipment for HT-GPC is specially made to stand high temperatures. HT-GPC allows the measurement of average MWs and MWDs of polymers that will not dissolve in GPC solvents at conventional GPC temperatures. For analysis at high temperature, it is necessary to prepare standards at the same experimental conditions as used to prepare the normal samples; the standards commonly used for high temperatures are polystyrene and polybutadiene, among others.

The effect of the temperature on the elution peak position is presented in Figure 17.5 for eight PS standards at three different temperatures [27]. When the samples are analyzed above room temperature, the elution peak presents a shift to lower values, which is indicative of the fact that the volume of the pore is also reduced as a result of the thermal expansion of the eluent and the packing materials. As can be seen, the elution time diminishes as the temperature increases in the column, an effect which is larger for a lower MW. The magnitude of the peak gets relatively small for the higher MW samples.

It is usually reported that the width of the elution peak decreases significantly as the column temperature increases, which is attributed to the facilitated mass transfer of the polymer chains. As a result of the reduced width, a better resolution is obtained in the chromatograms when high temperature SEC is used.

Polymers Characterized by HT-GPC A number of polymers can be characterized by GPC in 1,2,4-trichlorobenzene at an elevated temperature: polyethylene, polypropylene, poly(ethylene-vinyl acetate), poly(ethylene-methyl acrylate), polyethylene propylene diamine rubber, different types of butyl rubber, and poly(phenylene oxide). In Table 17.3 are presented some common polymers, as well

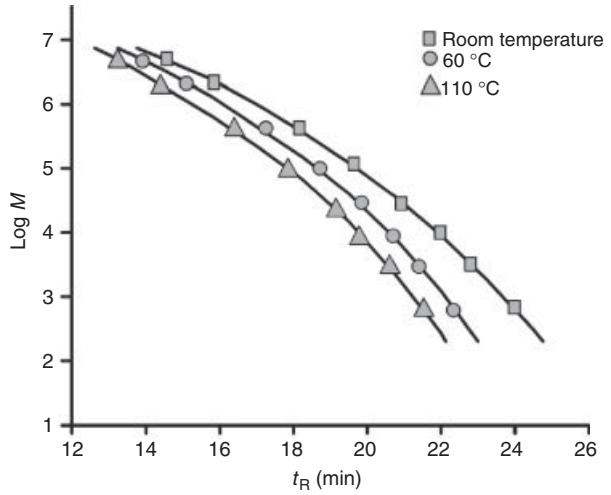

Figure 17.5 Effect of column temperatures on calibration curves of eight PS standards. *Source*: Reprinted with permission from Cho H, Park S, Ree M, Chang T, Jung JC, Zin WC. *Macromol Res* **2006**;14(3):383 [27]. Copyright 2006 The Polymer Society of Korea.

as the solvents used to dissolve them; as can be observed some of them require high temperature in order to be run by GPC. Most of the rubbers can be dissolved in toluene at 75 °C. Most of the amorphous polymers can be prepared at room temperature, but semicrystalline polymers require high temperatures to be dissolved.

Branching High temperature GPC equipment generally counts with different types of detectors such as refractive index, light scattering, and viscometer, among others; using these detectors it is possible to obtain the absolute MW, and in most cases it is not necessary to construct a calibration curve. A viscometer detector also provides information about the level of branching of a polymer; in fact, using this it is possible to obtain the index of branching (g'), which is defined by the following equation [28]:

$$g' = \frac{\eta_1}{\eta_b} \tag{17.3}$$

where η_1 is the intrinsic viscosity of the linear polymer and η_b is the intrinsic viscosity of the branched polymer (of the same chemical nature and same molecular weight).

Sample Preparation A small sample of polymer is weighed (10 mg) and placed in a 15-ml stainless steel vial. Then, 10 ml of 1,2,4-trichlorobenzene is added to the vial and the sample is placed in an oven at 120 °C for 3 h. A stabilizing agent, such as Irganox 1010, should be added to the solvent to avoid degradation of the polymer during the dissolution period. Once the polymer is solubilized, a stainless steel filter is placed on top of the stainless steel vial; the filter is pushed down, thus the solution is filtered; in this step, any contaminants are removed from the solution.

TABLE 17.3 Polymers Commonly Characterized by GPC and Conditions Used in the Analysis

Solvent	Polymer
Chloroform 30 °C	ABS
	PB
	PC
	Poly(ethyl acrylate)
	PS
Chloroform/hexa-fluoroisopropanol (98/2%) 25 °C	PET
	PBT
Tetrahydrofuran 25 °C	PB
	SBR
	TFA
Tetrahydrofuran 30 °C	Alquidalic resins
	Poly(acrylonitrile-methyl methacrylate)
	Cellulose acetate butyrate
	Cellulose acetate propionate
	Cellulose nitrate
	Cellulose propionate
	Cellulose triacetate
	Epoxy resins
	Phenolic resins
	Phenol formaldehyde resins
	PB
	Polybutene
	Poly(butadiene-styrene)
	PMMA
	Poly(propylene glycol)
	PS
	SAN
	Poly(styrene-α-methylstyrene)
	SBS
	PVA
	PVB
	PVC
Toluene 75 °C	Polyisobutylene
	Chlorinated rubber
	Silicone
Toluene 30 °C	PDMS
	PB
	Polyisobutylene
	Polyisoprene
	Poly(methyl acrylate)
1,2,4-Trichlorobenzene 140 °C	PE
	Chlorinated polyethylene
	EVA
	Acid methacrylic polyethylene
1,2,4-Trichlorobenzene 145 °C	UHMWPE
	PP

Abbreviations: ABS, acrylonitrile-butadiene-styrene terpolymer; PB, polybutadiene; PC, polycarbonate; PS, polystyrene; PET, poly(ethylene terephthalate); PBT, poly(butylene terephthalate); SBR, styrene-butadiene rubber; TFA, *N*-trifluoroacetylated polyamides; PMMA, poly(methyl methacrylate); SAN, poly(styrene-acrylonitrile); SBS, poly(styrene-butadiene-styrene); PVA, poly(vinyl acetate); PVB, poly(vinyl butyral); PVC, poly(vinyl chloride); PDMS, poly(dimethyl siloxane); PE, polyethylene; EVA, poly(ethylene-vinyl acetate); UHMWPE, ultra high molecular weight polyethylene; PP, polypropylene.

After this, the sample is ready to be injected into the GPC column. The filtration of the sample can be carried out by the equipment itself (automatically) or manually by the technician. The filtered solution has to be kept at high temperature to avoid the precipitation of the polymer. Once the sample is filtered, it is ready to be run by GPC. Samples must be injected at least four times to obtain statistically valid results of the MW.

17.4 MEASUREMENT OF INTRINSIC VISCOSITY

17.4.1 Introduction

The measurement of intrinsic viscosity is simple and inexpensive when compared with other measurements related to the polymer MW. However, it can be time consuming, even if modern semiautomatic instruments are used for that purpose. As mentioned in Chapter 1, measurements of intrinsic viscosity were historically important in establishing the concept of macromolecules [29].

The determination of the intrinsic viscosity of a polymer essentially requires the measurement of the flow time of a polymer solution through a glass capillary at different solution concentrations. A polymer solution passing through a capillary obeys the Poiseuille's law for laminar flow through capillaries, which indicates that the pressure drop ΔP is directly proportional to the viscosity η of the fluid [29, 30].

$$\Delta P = k\eta \tag{17.4}$$

where $k = 8Ql/\pi r^4$. Then, the viscosity can be expressed as

$$\eta = \frac{\pi \Delta P r^4}{8lQ} \tag{17.5}$$

where η is the viscosity of the polymer solution (poise), ΔP is the pressure difference of the fluid in the capillary (dyn/cm^2), r is the capillary radius (cm), l is the capillary length (cm), and Q is the volumetric flow rate through the capillary (cm^3/s).

In order to get a simpler equation, some considerations are made. The bulb volume in the viscometer is fixed; therefore, the flow rate Q is inversely proportional to the time between marks. Since ΔP is usually the hydrostatic pressure, which is proportional to the density ρ of the fluid, we have

$$\eta\alpha\ t\rho \Rightarrow \eta = At\rho \tag{17.6}$$

where A is a constant for a particular viscometer, which may be evaluated using liquids of known viscosity; t is time, and ρ is the density of the liquid.

The above equation is valid if the whole pressure difference applied across the capillary is used in overcoming viscous forces. However, the potential energy of the liquid column imparts kinetic energy to the fluid. In order to correct the contribution of the kinetic energy, as the length of the capillary increases, the radius decreases [31, 32].

Several methods exist for characterization of the solution viscosity or, more specifically, the capacity of the solute to increase the viscosity of the solution. That capacity is quantified by using one of several different measures of solution viscosity.

17.4.2 The Ubbelohde Capillary Viscometer

The Ubbelohde viscometer is the most common type of viscometer used for the determination of the intrinsic viscosity. It was originally introduced in 1937 [33] and is shown in Figure 17.6.

For the operation of the viscometer, a polymer solution of known concentration is put in the reservoir and aspirated to the upper bulb, usually by creating some vacuum in that chamber; then air is admitted so the solution flows down the capillary by gravity. The time for the liquid to flow between

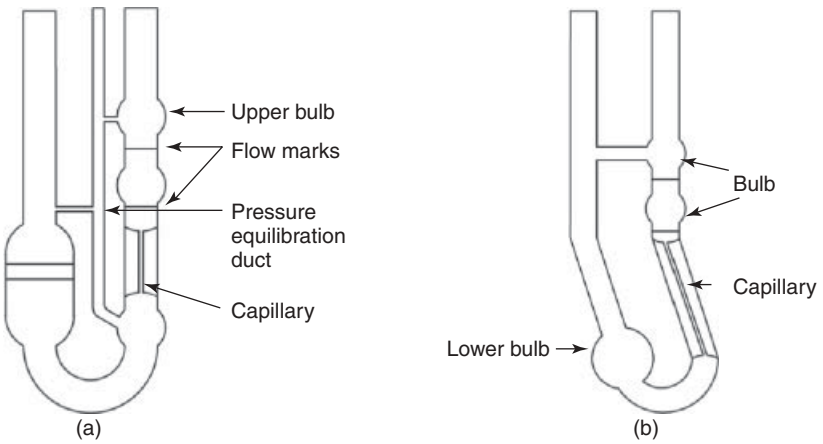

Figure 17.6 Illustration of two types of viscometers: (a) Ubbelohde and (b) Cannon–Fenske.

the two marks is recorded. This operation is repeated for increasingly dilute solutions of the same polymer/solvent. A duct parallel to the capillary allows pressure equilibration, so the flow of the fluid is only due to the hydrostatic head. Notice that the Cannon–Fenske viscometer [34] does not have the pressure equilibration duct, so it is not appropriate for accurate measurements of the intrinsic viscosity.

17.4.2.1 Measurement of the Intrinsic Viscosity The principle behind capillary viscometry is the Poiseuille's law, which states that the time of flow of a polymer solution (ps) through a thin capillary is proportional to the viscosity of the solution. The latter increases with increasing solution concentration. From Equation 17.6, the time of flow of the solvent (solv) or of the polymer solution will be proportional to the viscosity, and inversely proportional to the density:

$$t_{\text{solv}} = \frac{\eta_{\text{solv}}}{\rho_{\text{solv}}} \tag{17.7}$$

$$t_{\text{ps}} = \frac{\eta_{\text{ps}}}{\rho_{\text{ps}}} \tag{17.8}$$

It is convenient to define some terms related to the viscosity of polymer solutions:

η_{r} is the relative viscosity (or viscosity ratio according to the IUPAC), defined as the ratio

$$\eta_{\text{r}} = \frac{\eta_{\text{ps}}}{\eta_{\text{solv}}} \tag{17.9}$$

η_{sp} is the specific viscosity, which is defined as the ratio

$$\eta_{\text{sp}} = \frac{\eta_{\text{ps}} - \eta_{\text{solv}}}{\eta_{\text{solv}}} = \eta_{\text{r}} - 1 \tag{17.10}$$

η_{red} is the reduced viscosity (or viscosity number according to the IUPAC), which is defined as

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} \tag{17.11}$$

where c is the polymer solution concentration.

At the low polymer concentrations used in viscometry, $\rho_{\text{ps}} \approx \rho_{\text{solv}}$, therefore, from Equations 17.7–17.9, the relative viscosity becomes

$$\eta_{\text{r}} = \frac{t_{\text{ps}}}{t_{\text{solv}}} \tag{17.12}$$

By similar arguments, the specific viscosity can be expressed by the following equation:

$$\eta_{\text{sp}} = \eta_{\text{r}} - 1 = \frac{t_{\text{ps}} - t_{\text{solv}}}{t_{\text{solv}}} \tag{17.13}$$

Both η_{r} and η_{sp} depend on the polymer concentration. In fact, Flory proposed that the ratio η_{sp}/c (reduced viscosity) is a measure of the specific capacity of the polymer to increase the relative viscosity [35]. By extrapolating the reduced viscosity to zero concentration, the inherent properties of the polymer at hand are captured. Therefore the intrinsic viscosity is found as stated by Equation 17.14:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{\text{sp}}}{c} \tag{17.14}$$

17.4.2.2 Intrinsic Viscosity The intrinsic viscosity $[\eta]$, defined by Equation 17.14, as the limiting value of the ratio of the solution's specific viscosity to the concentration of the solute as the concentration approaches zero, reflects the capability of a polymer in solution to increase the viscosity of the solution.

Kraemer defined the intrinsic viscosity as [36]

$$\frac{\ln \eta_{\text{r}}}{c} = [\eta] + k_1 [\eta]^2 c \tag{17.15}$$

where k_1 is known as the *Kraemer constant*.

The intrinsic viscosity (or limiting viscosity number) can be obtained by measuring the relative viscosity at different concentrations and then taking the limit of the specific viscosity when the concentration is extrapolated to zero (Fig. 17.7). The behavior of the intrinsic viscosity with concentration depends on the nature of both the specific polymer molecule and the solvent. Since the intrinsic viscosity of linear polymers is related to the MW, for linear macromolecules intrinsic viscosity measurements provide a simple method for the determination of MW when the relationship between viscosity and MW is known.

Additionally, Huggins described the relation η_{sp}/c (reduced viscosity) as [37]

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} = [\eta] + k_2 [\eta]^2 c \tag{17.16}$$

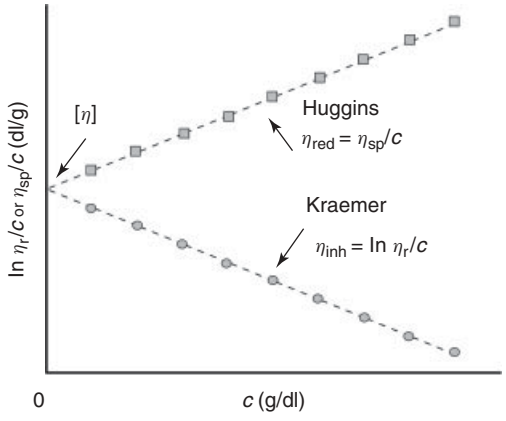

Figure 17.7 The Kraemer–Huggins plot to obtain the intrinsic viscosity, where the inherent viscosity is defined as $\eta_{\text{inh}} = \ln \eta_{\text{r}}/c$.

where k_2 is called the *Huggins viscosity constant* and is derived from the slope of the plot of reduced viscosity with c. This constant can be understood as a measure of solvent quality. For example, for polymers in a good solvent $k_2 \approx 1/3$, while in poor solvents k_2 values are in the range 0.5–1. Details of the values of this constant can be found in the literature [29].

The lines in Figure 17.7 come from plotting η_{red} from Equation 17.11, using Equation 17.13, for η_{sp} or plotting $[\ln(\eta_r)]/c$. The latter is also called *inherent viscosity*, η_{inh}, or logarithmic viscosity number (IUPAC). Both lines have the same intercept, which gives an estimation of $[\eta]$, the intrinsic viscosity.

Conventionally, the most common units used for concentrations in this type of measurements is g/dl (grams per deciliters, which is rather uncommon units in other fields), so $[\eta]$ is usually expressed as dl/g (units of inverse concentration according to Equation 17.14, since η_{sp} is dimensionless).

The intrinsic viscosity reflects the average interactions of single polymer molecules with the solvent and, if the molecule is considered to be spherical, $[\eta]$ is proportional to the volume of the molecule. In most of the cases, the configuration of polymer molecules in dilute solution roughly resembles a ball, whose size is characterized by the radius of gyration R_g. For polymers having a random-coil configuration, it is calculated that $R_g \propto M^{1/2}$, where M is the molar mass of the polymer. Thus, the relationship between intrinsic viscosity and molar mass is given by [38]

$$[\eta]_\theta = K_\theta M^{1/2} \tag{17.17}$$

This equation applies for polymeric solutions under "theta" conditions. Theta conditions are those at which excluded volume effects (expansion of the dimensions of the ideal coil) are exactly compensated by polymer solvent interactions (Chapter 25). The dependence between intrinsic viscosity and MW is given by the Mark-Houwink-Sakurada equation (see also Chapter 1):

$$[\eta] = K\overline{M_v^\alpha} \tag{17.18}$$

where K and α are two parameters that depend on the solvent, polymer, and temperature. Values of these coefficients for several polymers and solvents are presented in Table 17.4. More complete tables are reported in different polymer handbooks [39]. Thus, given an experimental measurement of the intrinsic viscosity in the laboratory, and the values of K and α reported in tables from the literature, one can obtain the viscosity-average molar mass of a polymer, $\overline{M_v}$.

The MW obtained in this way, $\overline{M_v}$, is higher that $\overline{M_n}$ and lower than $\overline{M_w}$; sometimes $\overline{M_v}$ can reach values very close to $\overline{M_w}$. An advantage of obtaining this average MW with capillary viscosimetry is that the equipment used (the viscometer) is very inexpensive in comparison to those used in other sophisticated techniques, and the measurements of flow time are very simple; the only drawback is the time consumed to prepare the samples at different concentrations and to run the samples in the glass viscometer, repeating the measurements a certain number of times.

The constant α in the Mark-Houwink-Sakurada equation can take values between 0.5 and 0.8, depending of the

TABLE 17.4 The Mark-Houwink-Sakurada Constants for Various Polymers in Selected Solvents

Polymer	Solvent	Temperature (°C)	$K \times 10^4$ $[\eta]$ (dl/g)	α	References
Polybutadiene (cis/trans ≈ 0.8), 8% vinyl	Tetrahydrofuran	25	4.57	0.693	[40]
Butyl rubber	Tetrahydrofuran	25	0.85	0.75	[40]
Nylon 66	*m*-Cresol	130	0.40	1.00	[40]
Nylon 6	*m*-Cresol	25	32	0.62	[40]
Polyethylene (LDPE)	*o*-Dichlorobenzene	138	5.06	0.70	[40]
Poly(ethylene terephthalate)	*m*-Cresol	135	1.75	0.81	[40]
Poly(methyl methacrylate) atactic	Acetone	25	0.96	0.69	[39]
Poly(methyl methacrylate) isotactic	Acetone	30	2.30	0.63	[39]
Poly(dimethyl siloxane)	*o*-Dichlorobenzene	138	3.83	0.57	[40]
Polypropylene	*o*-Dichlorobenzene	135	1.30	0.78	[40]
Polypropylene atactic	Benzene	25	2.7	0.71	[39]
Polypropylene isotactic	Biphenyl	125.1	15.2	0.50	[39]
Polypropylene syndiotactic	Heptane	30	3.12	0.71	[39]
Poly(acrylic acid)	Aq. NaCl (1 M)	25	4.15	0.63	[39]
Poly(methyl acrylate)	Acetone	25	1.98	0.66	[39]
Polystyrene atactic	Benzene	25	2.27	0.72	[39]
Polystyrene isotactic	Benzene	30	0.95	0.77	[39]
Poly(vinyl acetate)	Tetrahydrofuran	25	3.50	0.63	[40]
Poly(vinyl chloride)	Tetrahydrofuran	25	1.63	0.766	[40]
SBR (25% styrene)	Tetrahydrofuran	25	4.10	0.693	[40]

configuration that the macromolecule adopts in solution. Values closer to 0.8 indicate that the polymer is in a good solvent. If constants for a specific polymer–solvent system are not reported in the literature, they can be obtained experimentally using monodisperse polymers of known MW.

If Equation 17.18 is plotted in the log–log scale, the intercept will give the value of log (K) while the slope will provide an estimate of α. The slope is related to the shape of the polymer molecules and the polymer–solvent interactions. For a polymer under theta conditions (unperturbed random coil), $\alpha = 0.5$. For a polymer in a good solvent, $\alpha = 0.8$; while for rodlike polymers $\alpha = 2$ [41]. van Krevelen [41] also provides some criteria to estimate α, which is based on the solubility parameters of the polymer and the solvent.

It is important to point out that the Mark-Houwink-Sakurada equation does not apply to polymers with low MWs, as indicated in the literature [29].

Nowadays, the new GPC hardware can have different detectors coupled, such as viscosity detectors, which allow measurements *in situ* of the intrinsic viscosity of polymers as well as the constants K and α. Using this advanced equipment, one can obtain the MW and intrinsic viscosities of polymers in a very short time.

17.4.2.3 Detailed Sample Preparation and Measurement of Intrinsic Viscosity In order to obtain the intrinsic viscosity of a polymer in a dilute solution, different concentrations of a polymer in a solvent are prepared. A small amount of polymer is weighed and dissolved in a solvent during a few hours using a stirrer in order to improve the solubility of the polymer. It is recommended to prepare at least six different concentrations of a polymer in a solvent. The highest concentration could be in the order of 30 mg in 10 ml of solvent and the rest of the concentrations should be more dilute; however, the concentrations will depend on the type of polymer. There are different ASTM (American Society for Testing and Materials) methods recommended to measure the intrinsic viscosity of different polymers.

The solutions prepared, as well as the pure solvent, should be filtered to remove any impurities that could affect the results. The filters used are generally made of Nylon, Teflon, or cellulose acetate with a pore size of less than 5 μm.

Once the solutions are prepared, a thoroughly clean capillary viscometer is introduced into a bath of water or oil at controlled temperature. The viscometer containing the pure solvent is left at least for 20 min in the bath in order to reach thermal equilibrium. Once the temperature is stable, a chronometer is used to measure the time it takes for the solvent to flow between the two marks of the viscometer. This measurement is carried out at least seven times in order to obtain the average time of flow. Once the time of the solvent flow is measured, the solvent is removed from the viscometer and the previous procedure is repeated for the solution with the highest polymer concentration. Again, the sample is left for at least 20 min in the bath at controlled temperature and, upon reaching thermal equilibrium, the flow time measurements are carried out at least seven times in order to obtain the average flow time. The procedure is followed for all the polymeric solutions prepared. Once the flow times of the solvent and of the different solutions are registered, the data are plotted as described in the previous section. The inherent or reduced viscosity is plotted against concentration, and from the linear plot obtained, the intrinsic viscosity is obtained using the Huggings or Kraemer equations. Intrinsic viscosity is obtained by the extrapolation of the curve obtained to zero concentration (intercept with the y-axis). The plot obtained should be a straight line; if the curve obtained is not a straight line, more dilute solutions of the polymer should be prepared and the measurements repeated to obtain a linear behavior.

The intrinsic viscosity is commonly used in several polymer industries for estimation of the MW of certain polymers, especially poly(ethylene terephthalate) (PET) or Nylon. Once the intrinsic viscosity is known, the viscosimetric MW $\left(\overline{M_v}\right)$ of the polymer can be obtained using the values of K and α reported in the literature [39].

REFERENCES

1. Tswett M. Ber Deutsch ot Ges 1906;24:316.
2. Abraham MH. J Chromatogr A 2004;1061:113.
3. Mainhard JE. Science 1949;110:387.
4. Kuhn R, Lederer E. Naturwissenschaften 1931;19(14):306.
5. Moore JC, inventors; The Dow Chemical Company, assignee. US patent 3326875. 1963.
6. Lathe GH, Ruthven CRJ. Biochem J 1956;62:665.
7. Moore JC. J Polym Sci A 1964;2(2):835.
8. Schroder E, Muller G, Arndt KF. *Polymer Characterization*. 1st ed. New York: Hanser Verlag; 1989. p 167.
9. Grubisic Z, Benoit H, Rempp P. J Polym Sci Polym Lett 1967;5(9):753.
10. Sun T, Chance RR, Graessley WW, Lohse DJ. Macromolecules 2004;378(11):4304.
11. Sperling LH. *Introduction to Physical Polymer Science*. 2nd ed. New York: John Wiley and Sons Inc.; 1992. p 91.
12. Bender M. J Chem Educ 1952;29(1):15.
13. Rubin RJ. J Chem Phys 1972;56:5747.
14. Wei G. Macromolecules 1997;30(7):2125.
15. Chance RR, Banluklewicz SP, Mintz D, Strate GV, Hadjichristidis N. Int J Polym Anal Charact 1995;1(1):3.
16. Boyd RH, Chance RR, Strate GV. Macromolecules 1996; 29(4):1182.
17. Otocka EP. J Chromatogr A 1973;76(1):149.

18. McCormick HW, Brower FM, Kin L. Polym Chem 1959; 39(135):87.
19. Gehman SD. Ind Eng Chem 1952;44(4):730.
20. Montfort JP, Marin G, Monge P. Macromolecules 1986; 19(7):1979.
21. Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A. Macromolecules 1994;27(17):4639.
22. Sadao M, Susuki T. Anal Chem 1980;52(11):1625.
23. Holding SR, Vlachogiannis G, Barker PE. J Chromatogr A 1983;261:33.
24. Yamamoto S, Nomura M, Sano Y. J Chromatogr A 1987; 394(2):363.
25. Renn CN, Synovec RE. Anal Chem 1992;64:479.
26. Antia FD. Csaba Horváth. J Chromatogr A 1988;435:1.
27. Cho H, Park S, Ree M, Chang T, Jung JC, Zin WC. Macromol Res 2006;14(3):383.
28. Zimm BH, Stockmayer WH. J Chem Phys 1949;17: 1301.
29. Barth HG, Mays JW. *Modern Methods of Polymer Characterization*. 1st ed. New York: Wiley; 1991. p 2321.
30. Striegel AM, Yau WW, Kirkland JJ, Bly DD. *Modern Size-Exclusion Liquid Chromatography*. 1st ed. New York: John Wiley & Sons; 1979. p 163.
31. Cannon MR, Manning RE, Bell JD. Anal Chem 1960;32(3): 355.
32. Wagner RH. Anal Chem 1948;20(2):155.
33. Ubbelohde L. Ind Eng Chem Anal Ed 1937;9(2):85.
34. Cannon MR, Fenske MR. Ind Eng Chem Anal Ed 1938; 10(6):297.
35. Flory PJ. *Principles of Polymer Chemistry*. New York: Cornell University Press; 1953. p 309.
36. Kraemer EO. Ind Eng Chem 1938;30(10):1200.
37. Huggins ML. J Am Chem Soc 1942;64:2716.
38. Flory PJ. *Principles of Polymer Chemistry*. New York: Cornell University Press; 1953. Chapter 10.
39. Brandrup J, Immergut EH, Grulke EA, editors. *Polymer Handbook*. 4th ed. New York: Wiley; 1999.
40. Evans JM. Polym Eng Sci 1973;13(6):401.
41. van Krevelen DW, te Nijenhuis K. *Properties of Polymers*. 4th ed. Amsterdam: Elsevier; 2009.