Original Article
Bulletin of Pure and Applied Sciences.
Chemistry , Vol.43 C, No.1
January-June 2024: P.19-26

http://www.bpasjournals.com/chemistry
DOI: https://doi.org/10.52710/bpas-chem.8
Print version ISSN 0970 4620
Online version ISSN 2320 320X

Determination of The Molecular Weight and Intrinsic Viscosity of Polystyrene Using Viscometric Method

Navneet Kumar

Author's Affiliations:
Associate Professor, Department of Chemistry, Faculty of Engineering, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh 244001, India.
E-mail: navkchem@gmail.com, drnavneet.engineering@tmu.ac.in

***Corresponding Author: Navneet Kumar,** Associate Professor, Department of Chemistry, Faculty of Engineering, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh 244001, India.
E-mail: navkchem@gmail.com

ABSTRACT
This study focuses on the determination of the molecular weight and intrinsic viscosity of polystyrene utilizing a viscometric method. Polystyrene are widely employed in various industrial applications, and understanding their molecular characteristics is crucial for optimizing their performance. The experimental approach involves the preparation of polystyrene with varying compositions. A series of solutions is created by dissolving these blends in a suitable solvent, and their viscosities are measured at different concentrations. The intrinsic viscosity is determined by extrapolating the viscosity data to zero concentration. The Mark-Houwink-Sakurada equation is employed to establish the relationship between intrinsic viscosity and molecular weight. By fitting experimental data to this equation, the molecular weight of the polystyrene is determined. This method offers a reliable and cost-effective approach for characterizing the molecular properties of polymer. The results provide valuable insights into the molecular weight distribution and intrinsic viscosity of the polystyrene, aiding in the optimization of processing conditions and end-use applications. Additionally, the viscometric method outlined in this study presents a practical and efficient technique for assessing the molecular characteristics of polymer blends, with potential applicability to other polymer systems.

Keywords: Polystyrene, Molecular Weight, Intrinsic Viscosity, Ubbelohde Viscometer

How to cite this article: Kumar N. (2024). Determination of The Molecular Weight and Intrinsic Viscosity of Polystyrene Using Viscometric Method. *Bulletin of Pure and Applied Sciences-Chemistry,* 43C (1), 19-26.

1. INTRODUCTION

Polymers like simple molecules can dissolve in common solvents. They are composed of functional groups as chemically reactive; they exhibit colligative properties and at specific wavelength can absorb energy. However, unlike simple organic molecules, they are made up of smaller monomer units of different sizes. These changes in the degree of polymerization, give rise to molecules with different molecular weights and different molecular weight distributions. Polymers can be characterized as (i) chemical identity of the repeat unit, (ii) character of the end group, (iii) nature and extent of cross linking, (iv) solubility, and (v) colligative properties. Absolute methods allow the direct computation of polymer molecular weight from measured quantities without assumptions about the chemical and/or physical properties of tested polymer molecule [1]. The equivalent techniques, although direct calculation of molecular weight can be made from measured data requires knowledge of the chemical composition of the polymer molecule. The relative methods, measured properties that depend on the chemical and physical composition of the polymer structure; requiring molecular weight curves of polymer standards of the same chemical and physical structure as that of the characterized polymer to be established [2].

However, all synthetic polymers contain polymer chain of uneven length; i.e they are polydispersed, and as such, molecular weight is not a single value but often described as average molecular weight. The average molecular weight can be expressed in different ways such as number average molecular weight (Mn), weight average molecular weight (Mw), viscosity average molecular weight (Mv), and higher average molecular weight (Mz, Mz+1). The choice of technique for molecular weight assesment is influenced by factors such as (i) information required, (ii) operative region, (iii) cost effectiveness, and (iv) experimental conditions and requirements.

Polymers are used in many engineering and chemical industries, so studying the cause of various weathering conditions on the mechanical and physical properties of these materials has become necessary to know the extent to which such materials can tolerate such conditions: high temperatures, corrosive solutions, and all corrosive bases, such as radiation. The consequence of weathering conditions and decomposition processes for polymers can occur during any stage of polymer life, as it can occur during: manufacturing processes, moulding and shaping processes and finally during use. Polymer solvents have a key role in studying the structure of the polymeric chain, as the solubility in the solvent has a important consequence on its rheological behavior, starting with the stretching of the polymer chain. A number of factors control the flowing nature of a polymer solution, which makes it difficult to explain the viscosity measurements and are made by means of dilute solutions for the purpose of reducing interactions between the molecules of polymer. So, just the reactions taking place between the polymer and the solvent are specified [3].

Polystyrene is a cheap, transparent polymer that is significant and widely used plastics and is suitable for a multiplicity of applications. As consequence of good resistance of polystyrene to radiation through which the molecules are supplied with energy, a structural change occurs which leads to a change in the average molar mass. The average molar mass is of great significance in the revision of polymers' behavior. It characterizes the length of molecule chains, and this is of huge significance and its importance lies in the processing and its overall performance. The physically and chemically properties of product are described by determining the average chain length, or the socalled (average degree of polymerization). Therefore, polymer chains length is very important. The method of dissolving the polymer in a suitable solvent is considered very significant scientific methods in calculating the molecular weight and for this reason, by measuring the viscosity can be calculated such as the average molar mass [4].

Molecular weight

The molecular weight of polystyrene can vary depending on the polymerization process and the desired charateristics of final product. However, the average molecular weight of commercially available polystyrene typically falls within the range of 100,000 to 200,000 grams per mole (g/mol). It's important to note that this is an average molecular weight, and polymer may have a distribution of molecular weights, resulting in a polydispersed polymer. Polystyrene is a synthetic polymer made from the polymerization of styrene monomers. It is a critical parameter that affects the material's physical and mechanical characters, like as its strength, flexibility, and thermal characteristics [5]. Different grades of polystyrene may have variations to suit specific applications, including packaging, insulation, and various consumer goods [6].

Molecular weight in polymers are 4 types:

a) One metric used to characterize the molecular weight distribution in polymers is the number average molecular weight (Mn). $Mn = \sum Ni \cdot Mi / \sum Ni$ is the formula, and it is defined as the total number of molecules divided by the sum of the products of the number of molecules

(Ni) in each molecular weight (Mi) percent. In this case, the molecular weight of the i-th fraction is Mi, the number of molecules in the i-th molecular weight fraction is Ni, and the average molecular weight is Mn. A variety of experimental approaches, including light scattering, gel permeation chromatography (GPC), and other size exclusion chromatography methods, can be used to quantify the Mn. These techniques enable the identification of the molecular weight distribution and separate polymer chains according to their size. In polymer research and engineering, knowing the average molecular weight is crucial because it affects the mechanical and physical characteristics of polymers, including their viscosity, tensile strength, and other performance attributes [9].

b) An additional metric for characterizing the molecular weight distribution in polymers is the weight average molecular weight (Mw). It considers the total number of polymer molecules as well as the molecular weights of each one separately. The weight average molecular weight can be computed using the formula $Mw= \sum wi\cdot Mi/\sum wi$. In this case, wi is the weight fraction of the i-th molecular weight fraction (proportional to the mass of polymer in that fraction), and Mw is the weight average molecular weight. The i-th fraction's molecular weight is denoted by Mi. Additionally, the Mw can be ascertained empirically by means of methods such as size exclusion chromatography (SEC) or gel permeation chromatography (GPC). By using these techniques, polymer chains are separated according to their size, and information on molecular weight and distribution is obtained by eluting the chains through a chromatographic column. The weight average molecular weight, which represents the impact of longer polymer chains on the material's properties, is crucial for comprehending the entire behavior of polymers, including their rheological qualities, processing traits, and mechanical performance [11].

c) Another metric for describing the molecular weight distribution in polymers is the Z-average molecular weight (Mz). This measure, which is expressed as $Mz= \sum wi\cdot Mi3/\sum wi\cdot Mi2$, takes the molecular weight's third power into account while determining average. In this case, the molecular weight of the i-th fraction is Mi, the weight fraction of the i-th molecular weight fraction is Wi, and the Z-average molecular weight is Mz. Ms. Gel permeation chromatography (GPC) and size exclusion chromatography (SEC), which separate polymer chains according to size, can be used experimentally to evaluate Mz. The distribution of molecular weights in the polymer sample can be inferred from the elution profiles produced by these techniques, which can also be used to determine Mz. In polymer research, knowing the Z-average molecular weight is crucial because it provides insight into the existence and effects of very high molecular weight species, which can have a big impact on a material's behavior and properties [12].

d) An other technique for determining the molecular weight of polymers is the viscosity average molecular weight (Mv). the assessment of a polymer's intrinsic viscosity, which quantifies its capacity to raise a solvent's viscosity. The Mv is measured by the Mark-Houwink equation $[\eta]=K\cdot M^{\alpha}$. Where, $[\eta]$ is the intrinsic viscosity, K and α are constants specific to the polymer-solvent system, M is the molecular weight. The Mv is then calculated by the relationship, $Mv =K' \cdot[\eta]$ where K′ is a constant [13].

It is particularly useful for high molecular weight polymers, and the average molecular weight depend on the polymer's hydrodynamic volume in solution. The experimental determination of Mv involves measuring the intrinsic viscosity of polymer solutions at various concentrations and extrapolating to zero concentration. The intrinsic viscosity can be obtained from the slope of the plot of relative viscosity versus concentration. While Mv is a useful parameter for describing the molecular weight of polymers, it is important to note that different methods (such as number average, weight average, and viscosity average) may yield different values depending on the polymerization method and the specific techniques used for measurement. Researchers often use a combination of methods to obtain a comprehensive understanding of a polymer's molecular weight distribution [14].

As the above, it can be easily reprents the molecular weights in a heterogenous polymer in Figure 1.

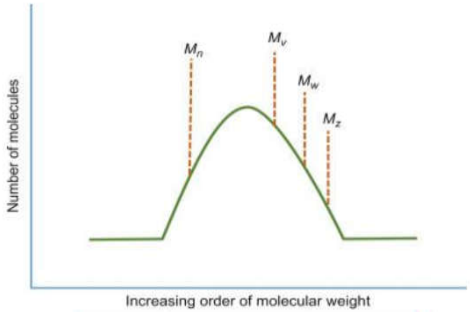

Figure 1: Graphical presentation of Molecular weights in heterogenous polymer

Polydispersity
Polydispersity is a measure of the distribution of molecular weights in a polymer sample. In other words, it quantifies how much the sizes of polymer chains in a sample vary. A polymer with a low polydispersity has a narrow distribution of molecular weights, meaning that most of chains have similar sizes. Scondary, a polymer with a high polydispersity has a broader distribution, indicating a wider range of molecular weights. Polydispersity can be characterized by a parameter known as the polydispersity index (PDI) or dispersity (Đ). It is calculated using the formula Đ= Mw/ Mn. Where, Mw is the weight average molecular weight, Mn is the number average molecular weight. The polydispersity index provides a numerical value that indicates the broadness or narrowness of the molecular weight distribution. If Đ is close to 1, it suggests a relatively narrow distribution, while higher values of Đ indicate a broader distribution. Polydispersity can have significant effects on the properties and performance of a polymer. As processing properties- polymers with thin molecular weight distribution often exhibit better processing properties, like as more predictable melt viscosity and improved melt stability during manufacturing processes. In mechanical properties, the polydispersity can impact its mechanical properties. For certain applications, a thin molecular weight distribution may be desirable to achieve consistent and predictable material behavior. In applications where polymer properties are critical, such as in biomaterials or electronic devices, controlling polydispersity becomes crucial to achieving the desired performance characteristics [15].

Polydispersity is influenced by the polymerization method, reaction conditions, and the choice of catalysts and solvents. Different polymerization techniques and strategies may be employed to control or narrow the molecular weight distribution depend on the desired properties of the final polymer product. Polymers have been producing polydispersity indices ranging from 1.0 to 1.2 in recent years. As the molecular weight differences in the structure are asked to be condensed to minimal level indicated in Figure-2, this rate of heterogeneity has been gradually decreased.

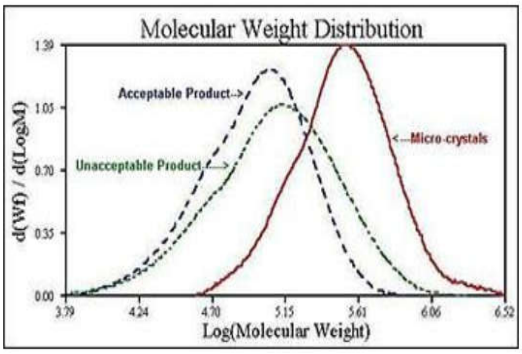

Figure 2: The molecular weight distribution

Viscosity and mechanical properties: a relationship

The viscosity and mechanical properties in polymers is complex and depends on different factors, including molecular weight, molecular weight distribution, temperature, shear rate, and the specific polymer chemistry. Viscosity and mechanical properties are interrelated in polymers, and understanding this relationship is crucial for designing materials with desired performance characteristics. High mechanical values are ideal, while the viscosity increases continuously as the molecular weight increases, the mechanical values crawl after a certain molecular weight. Because the high viscosity makes the material difficult to mold, an optimization between these values is required [16]. This material has a molecular weight of 10000-1000000 g/mol. The aforementioned data is displayed in Figure 3.

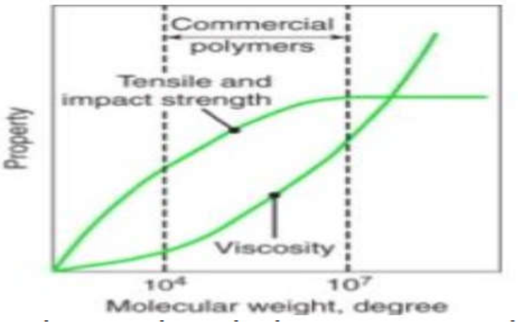

Figure 3: Representation-viscosity and mechanical properties

2. MATERIALS AND METHODS

The molecular size is the essential distinguishing properties of the poly- meric materials. The properties that have enabled these materials to be used in a diversity of applications derive mainly from their macro-molecular nature. These polymeric materials (thermoplastics and uncured thermosetting resins and elastomers) consist of an assembly of molecules having a distribution of molecular sizes, i.e., they are polydisperse. For full characterization of these polymeric materials, it is essential to have some means of defining and determining their molecular weights and molecular weight distributions. For instance, Colligative property measurements to determine number average molecular weight [17-18]. ($\overline{M}_n$) of the polymers. Light scattering techniques are used to determine the weight average molecular overline ($\overline{M}_w$) of the polymers and Solution viscosity measurements are used to measure the viscosity average molecular weight overline $\overline{M}_v$ of the polymers. The objectives of this study are to assesment the viscosity-average molecular weight and the intrinsic viscosity of polystyrene blends by Ubbelohde viscometer. Toluene was the suitable solvent for producing polystyrene in this investigation, and Table 1 shows its fixed value.

Table 1: Equation constants for various solvent-polymer relationships

Polymer & solvent system	**K x 10^3mL/g**	α
PMMA-Acetone	7.70	0.70
PMMA-Benzene	5.20	0.76
PMMA-Toluene	7.0	0.71
Poly vinyl acetate-Acetone	10.2	0.72
Poly vinyl acetate-Benzene	56.3	0.62
Poly vinyl acetate-Acetonitrile	41.5	0.62
Poly vinyl alcohol-Water	45.3	0.64
Poly styrene-Benzene	10.6	0.735
Poly styrene-Toluene	**11.0**	**0.725**

Viscosity of polymer samples is measured by weighing them using a sensitive balance. On the precision scale, the samples (0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g) were weighed in turn. Each sample was prepared using toluene as the solvent, and the amount of toluene used was quantified in a measuring cylinder. Measured toluene, polystyrene, and a magnetic stir bar that ensures the mixture is homogenous are added to the conical flask along with other necessary ingredients for the solution preparation and solvent maintenance steps. To ensure airtightness, the flask was sealed with toluene, a volatile substance. The intended concentration and the obtained concentration vary when there is a toluene loss. This also produces inaccurate outcomes. To achieve a homogenous solution, the flask was mounted on a magnetic stirrer that was set to 250 revolutions per minute at room temperature. Following the homogeneity of the solutions, the flasks were removed from the magnetic stirrer and a viscometer was used to measure the mixtures' viscosities [7].

An automatic system Ubbelohde capillary type viscometer, which enables the reading of flow times of the sample taken automatically without requiring a timer, was used to test intrinsic viscosity. The measurement was done at 25 ± 0.1°C and the capillary number is 531/10 I. Solvent was added to the measurement until five successive values deviated from the mean value by no more than 0.3 seconds. The flow rates of five distinct polystyrene solution concentrations were then noted.

The viscosity of a polymer solution depends both on concentration and on the average molecular size of the sample (and hence the molecular weight). The effective size of the molecules depends on the extent of interactions with the solvent. The polymer molecules assume expanded conformations in good solvents. But as the solvent becomes poorer, intermolecular interactions become more significant until for theta solvents the chains assume their unperturbed dimensions [8]. Thus the solution viscosity shows quite different dependence on molecular weight in different solvents.

Let, d_0, t_0 = density and flow time respectively of a solvent between two marks in a standard capillary of a viscometer,

d_c,t_c = density and flow time respectively of a series of dilute polymer solutions of known concentrations (C),

η_0 = viscosity of the pure solvent,

ηc = viscosity of dilute polymer solutions of known concentration (C),

Then, Relative viscosity (η_r) is defined as: $\eta_r = \eta_c / \eta_0$

And specific viscosity (η_{sp}) is defined as: $\eta_{sp} = \eta_r - 1 = \eta_c / \eta_0 - 1 = \eta_c - \eta_0 / \eta_0$

Moreover, $\eta_{sp} = \eta_c - \eta_0 / \eta_0 = d_c t_c - d_o t_o / d_0 t_0$

The intrinsic viscosity $[\eta]$ describes the ability of polymer molecules to increase the viscosity of the solvent in the absence of any intermolecular interactions.

From the Huggins equations: $\eta_{sp}/C = k' [\eta]^2 c + [\eta]$

Thus, the intrinsic viscosity for the polymer/solvent system is obtained by plotting η_{sp} /C versus C and extrapolating to zero concentration.

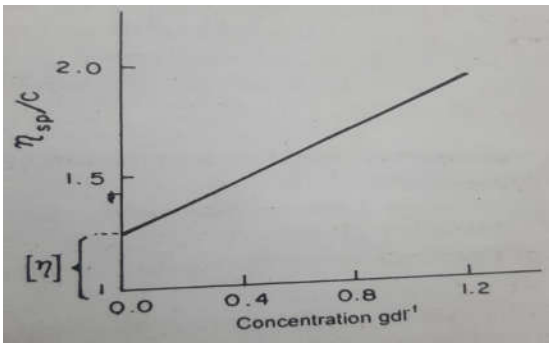

Figure 4: Dilute solution visconmetry: Huggins plot of (η_{sp}/C) against concentration.

The first term in the Huggins equation represents the interactions between different molecules in the solution. The viscosity so calculated is then used to determine M_V through the Mark-Houwink equation, $[\eta] = K\ (\overline{M}_v)^\alpha$. Where K and α are empirical constants for the particular polymer-solvent system. It is to be kept in mind that even for a particular polymer-solvent combination, effects such as chain branching influence the variation of $[\eta]$ with $\overline{M}_v$. Thus the empirical parameters k and a may not be constant for the same nominal polymer type. As the values of & and vary solvent and temperature; so care should be taken in interpreting values of molecular weight from solution viscosity measurements [10]. In general, $\overline{M}_v$, will be close to, but somewhat lower, than $\overline{M}_w$.

3. RESULTS AND DISCUSSION

Using an Ubbelohde viscometer, the molecular weight of the polymer was determined. This method yielded the viscosity average molecular weight. This material was selected primarily because of its extensive applicability in technical practice. Since polystyrene is a living polymer, its mechanical characteristics can be altered in different directions. This is especially true with anisotropic materials. The specific, intrinsic, and relative viscosities were calculated using the results. Finally, the Mark-Houwink equation $[\eta]=K\ (\overline{M}_v)^{\alpha}$ is applied using the computed intrinsic viscosity. Where M is the molecular weight, α is the constant for the specific polymer solvent temperature system, and η is the inherent viscosity. The molecular weight was ascertained following the viscometer method's determination of the inherent viscosity value. An evaluation was conducted on the intrinsic viscosity [η]. To do this, the ratio between the flow times of the polymer solution (t) and the pure solvent (t_0) was used to compute the relative viscosity (η_r). A specific gravity bottle was used to determine the density of tolune.

The specific viscosities of different solutions are calculated by using the formula $\eta_{sp}= d_ct_c-d_0t_o/d_ot_o$. Report the results of these calculations in Table 2 as given below:

Table 2:

Concentration(C)	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
Density	0.345	0.388	0.31	0.302	8.029
Specific viscosity(η_{sp})	0.52	0.61	0.70	0.78	0.86
(η_{sp}/C)	2.60	1.50	1.16	0.97	0.86

Extrapolate the calculated values of η_{sp}/C at zero concentration and get the value of intrinsic viscosity [η]. After the calculations, the average molecular weight of a polystyrene sample from the Mark-Houwink equation was found to be 53.3 gm/mole. The relationship between polystyrene concentration (C) and intrinsic viscosity (η_{sp}/C) in mixed toluene solvents with varying volume ratios at 25°C. Across the complete concentration range, η_{sp}/C and C may be seen to have a linear relationship. The intrinsic viscosity of polystyrene in mixed solvents can be found by extrapolating to zero concentration. It is observed that in mixed solvents with a reduced toluene ratio, the intrinsic viscosity of polystyrene increased.

4. CONCLUSIONS

A detailed investigation was conducted into the viscometric behavior of polystyrene in a mixed solvent of toluene and with temperature. The intrinsic viscosity of polystyrene was observed to increase in the mixed solvent with a greater ratio of toluene, in the intrinsic viscosity vers concentration. This finding suggests that the polymer–solvent interaction increased in the mixed solvent with a higher ratio of toluene. Theoretically, the specific viscosity vers concentration of polystyrene in the solvent can be transformed to obtain the correlation between the intrinsic viscosity of polystyrene at finite concentration and the concentration of polystyrene in solution, as discussed in the paper. Viscosity was found to decrease as polystyrene content in the solution increased, suggesting that the polymer's dimensions shrank in concentrated solution. A constant molecular weight cannot be mentioned in synthetic polymers because they are not made of the same chains as crystalline atoms or molecules. Additionally, a variety of production-related factors may have an impact on the molecular weight values that are obtained. The typical molecular weight of polystryne produced using various methods ranges from 10 to 40 gm/mole. Since the mechanical characteristics will improve with a regulated rise in value. The findings show that the molecular weight is more than what is considered to be the industrial range.

Acknowledgement
We wish to express our cordial thanks to Prof. R. K. Dwivedi, Principal, Faculty of Engineering, Teerthanker Mahaveer University, Moradabad for their encouragement and providing the requires.

REFERENCES

1. A. Rudin (1999). Mechanical properties of polymer solids and liquids, in: A. Rudin (Ed.), Elements of Polymer Science and Engineering, second ed., Academic Press, San Diego, 1999, 377_443.

2. Al-Azzawi AH, Entir EM. (2013). Study the effects of bromothymol blue material on the optical properties for polystyrene (PS). Baghdad Sci J. 10(1), 56-63. https://doi.org/10.21123/bsj.2013.10.1.56-63.
3. Bercea M, Wolf BA. (2018). Intrinsic viscosities of polymer blends: sensitive probes of specific interactions between the counterions of polyelectrolytes and uncharged macromolecules. Macromolecules. 51(19), 7483-90. https://doi.org/10.1021/acs.macromol.8b01422
4. Chuah, H. H., Lin-Vien, D., & Soni, U. (2001). Poly (trimethylene terephthalate) molecular weight and Mark–Houwink equation. Polymer, 42(16), 7137-7139.
5. F. Behrouzian, S. M. Razavi, H. Karazhiyan (2014). Intrinsic viscosity of cress (Lepidiumsativum) seed gum: effect of salts and sugars. Food Hydrocolloid. 35, 100-105.
6. H Yang , P Zhu, Y Xie, X Zhang, G Li. (2000). Viscometric study of polystyrene in mixed solvents and with varying temperature. Polymer. 41(2), 499-504.
7. J.L. Schultz, E.S. Wilks (2000). Nomenclature of Polymers, Encyclopedia of Polymer Science and Technology, Wiley, Hoboken, NJ.
8. Kumar A, Gupta RK. (2018). Fundamentals of polymer engineering. CRC Press; 616. https://doi.org/10.1201/9780429398506
9. Kumar V, Chaudhary B, Sharma V, Verma K. (2019). Radiation Effects in Polymeric Materials. Springer International Publishing. 8, 412. https://doi.org/10.1007/978-3-030-05770-1
10. L.W. McKeen (2012). Permeability Properties of Plastics and Elastomers, third ed., William Andrew Publishing, Oxford, 21_37.
11. M. Chanda (2013). Introduction to Polymer Science and Chemistry: A Problem-Solving Approach, second ed., CRC Press, Boca Raton, FL, p. 29.
12. Maafa IM . Pyrolysis of polystyrene waste: A review.Polymers. 2021; 13(2): 225. http://doi.org/10.3390/polym13020225.
13. Minagawa, T., Okamura, Y., Shigemasa, Y., Minami, S. and Okamoto, Y. (2007). Effects of molecular weight and deacetylation degree of chitin/chitosan on wound healing, *Carbohydrate Polymers*, 67, 640–644.
14. Nabhan, Baydaa Jaber et. al. (2023). Determination of Molecular Weight and Viscosity of Irradiated Polystyrene. Baghdad Science Journal. 20(3 Suppl.), 1139-1145 https://dx.doi.org/10.21123/bsj.2023.8111
15. R. Pamies, J. G. H. Cifre, M. D. C. L. Martínez, J. G. de la Torre (2008). Determination of intrinsic viscosities of macromolecules and nanoparticles. Comparison of single-point and dilution procedures, Colloid Polym. Sci. 286(11), 1223-1231.
16. Raouf RM, Nabhan BJ, Ayash AA. (2020). Evaluation the influence of cesium 137 source on some physical properties and molecular weight of poly vinyl acetate at room temperature. Mater Today Proc. 2020; Jan 1;20. https://doi.org/10.1016/j.matpr.2019.09.171
17. Solyman WA, Buni M S, Ali SA. (2013). Effect of GammaRay and Temperature on the Viscosity of Polystyrene. J Educ Sci. 26(1): 40-8. https://doi.org/10.33899/edusj.2013.89661
18. T. Bel, C. Arslan, N. Baydogan (2019). Materials Chemistry and Physics, 221, p. 58-67.

****