Comprehensive Journal of Science

Volume (10), Issue (38), (Dec, 2025)

ISSN: 3014-6266



مجلة العلوم الشاملة

المجلد (10) العدد 38 ديسمبر 2025 ادصد: 6266-3014

DETERMINATION OF VISCOSITY-AVERAGE MOLECULAR WEIGHT USING INTRINSIC VISCOSITY MEASUREMENT

Rabeeah, H. Sultan¹

¹Department of Chemical Engineering, Faculty of Engineering, University of Sabrath, Sabrath, Libya

email: rabia86sultan@gmail.com

Received: 13-11-2025; Revised: 20-11-2025; Accepted: 26-11-2025; Published: 8-12-2025

Abstract

In the present work, two types of polymers are polystyrene (PS) and polydimethylsiloxane (PDMS) were used, where Molecular weight of polymers can be determined by different techniques such as intrinsic viscosity measurement. Determination of molecular weight by intrinsic viscosity measurement is a simple method for characterization of polymers. Different concentrations of polymers were prepared and measurement was done at room temperature. The flow time data was used to calculate the intrinsic viscosity by extrapolating the reduced viscosity to zero concentration. The value of intrinsic viscosity was then recalculated into the viscosity-average molecular weight using **Mark-Houwink equation**. The results were obtained to calculate the viscosity average molecular weight of both types of polymers respectively, PS is (97,223.05) and PDMS is (100,359.98) and are considered good results.

keyword: Ostwald Viscometer, viscosity average molecular weight, intrinsic viscosity, polymer.

1- Introduction

A polymer is a large macromolecule built from a repetition of smaller chemical units called monomers. Proteins and polysaccharides are natural polymers whereas commonly used plastics and adhesives are synthetic polymers. As shown in Figure (1), the polymer could be linear, branched or cross-linked [1].

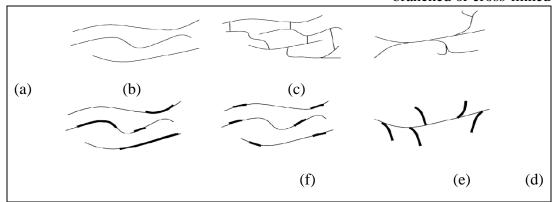


Figure (1): polymer structures. (a) linear (b) cross —linked (c) branched polymer (d) randomly distributed (e) block and (f) grafted copolymer[1].

The polymer molecules are essentially strings of atoms connected to each other via covalent bonds. However, the polymer molecules have the ability to physically associate and interact with spatially separated regions in a solution [2]. They can induce and transfer the effects such as a change in stress and structure from one region to another due to attractive interactions between certain regions of different polymer molecules and formation of three-dimensional networks. By incorporating more than one type of monomer in the same macromolecule, one can produce a polymer that exhibits more than one kind of affinity [2]. Therefore, the addition of small amounts (tens of parts per million by weight) of polymer to flow results in the reduction of skin friction in turbulent flows. This phenomenon is known as drag reduction and was discovered by Toms [3]. Since that time, interest in drag reduction using polymeric materials has grown because of its wide range of industrial applications.

- 1. The polymers insoluble in crude oil or in any it is a fraction, without affecting on its specification.
- 2. The polymer cannot be precipitated on the wall of the pipes.
- 3. The polymer form a homogeneous mixture with the crude oil or their fractions.
- 4. The polymer should be stable in the range of used temperature.
- 5. The polymer has high activity at low concentrations in the range of two ppm.
- 6. Uses of polymer in drag reduction of flowing crude oil depends on solubility of polymer in the solvent when the molecules of solvent are diffuse slowly through the polymer to produce jelly state and strong bonds between polymer and crude oil that follow vanish jelly state gives an actual solution is introduced when the mixing and heating are used to increase this process [4].

Molecular weight (MW) is one of the most fundamental parameters in characterizing a polymer. Molecular weight of polymers can be determined by different techniques, such as Gel Permeation Chromatography (GPC), Static Light Scattering (SLS) and intrinsic viscosity measurement. GPC is the most powerful technique for characterizing the molecular weight of polymers. However, it is a relative method and needs molecular weight standards for calibration to obtain the relation between elution volume and molecular weight. One of the simplest and rapid methods for determining the molecular weight of polymer is viscosimetry, although this is not an absolute method and requires the determination of constants. The intrinsic viscosity, η as function of average molecular weight, M is represented by Mark-Houwink-Sakurada equations[5]. The goals of this study are to determine the viscosity-average molecular weight and intrinsic viscosity of Ostwald viscometer.

2- Types of polymers using in work

2.1 Polystyrene (PS)

It Formed from monomers of Styrene Polymerization initiated by heat or catalyst and is commercially available over a wide range of molecular weight. The major application of PS are plastics, packing, insulation, food containers, disposable cutlery, electronic casings, toys and piping. Furthermore, PS has several properties of special interest such as colorless, hard, brittle plastic and it is a thermoplastic melts to a liquid when heated, and freezes to brittle glassy state when cooled, this property allows for PS to be molded and extruded [6]. Figure (2) illustrates the structure of the repeating unit of PS.

Figure (2): The structure of the repeating unit of PS[6].

Manufacturer information [7]:

Trade name: PS (Styrofoam)

Class: Vinyl polymers

Manufacturer: The Dow Chemical Company USA and others

Molecular weight: in the range of $(4-52)\times10^4$

Structure:

-CH −CH 2-n C 6H5

2.2 - Polydimethylsiloxane (PDMS)

PDMS consists of fully methylated linear siloxane polymers containing repeating units of the formula (CH3)₂SiO, with trimethylsiloxy end-blocking units of the formula (CH3)₃ SiO. The major applications of PDMS are release agents, rubber molds, sealants and gaskets, surfactants, water repellents, adhesives, foam control agents, biomedical devices and cosmetics, dielectric encapsulation, glass sizing agents, greases, hydraulic fluids, heat transfer fluids, lubricants, fuser oil, masonry protectants and process aids. Furthermore, PDMS has several properties of special interest such as thermal stability, low temperature performance and minimal temperature effect, good resistance to UV radiation, excellent release properties and surface activity, high permeability to gases, good damping behavior, antifriction and lubricity, hydrophobic and physiological inertness, shear stability, weak intermolecular forces, and excellent dielectric strength [6].

Manufacturer information[6]:

Trade name: PDMS poly[oxy(dimethylsilylene)]

Class: Polysiloxanes, di-methyl silicones and siloxanes

Manufacturer: Dow Corning © 200 fluid; Wacker SWS101 fluid; Baysilone © M fluid.

Molecular weight: in the range of $(67 - 117) \times 10^3$

Structure: —[(CH₃)₂Si—O—]n

3- Experimental work:

3.1 Material

In the present work, two types of commercial polymers, polystyrene (PS) and polydimethylsiloxane (PDMS), were used to determine the viscosity-average molecular weight and intrinsic viscosity. Various polymer solution concentrations were prepared to study their effects on viscosity. Toluene (C₇H₈), with a purity 99% was used as the solvent throughout the experiments.

3.2 Viscometer

Furthermore, for measurement of the Intrinsic viscosity for the polymer was examined using an automatic system Ostwald capillary type viscometer ASTM- 1p show in Figure (3), which allows the reading of flow times of the sample to be taken automatically with using a stopwatch. The Ostwald viscometer number 7195 and constant (c) is $0.007434 \, (\text{mm}^2/\text{s})/\text{s}$, made in England. Units of Kinematic Viscosity are: $1 \text{cSt} = 10^{-6} \, \text{m}^2/\text{s} = 1 \, \text{mm}^2/\text{s}$.

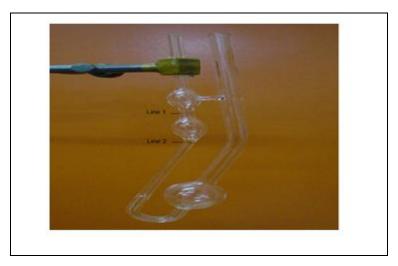


Figure (3): Viscometer of Ostwald.

3.3- Experimental Procedures

3.3.1- Determination of Polymer Average Molecular Weight

A- Intrinsic Viscosity Determination

The viscometer of Ostwald allows to determine the liquid viscosity coefficient According to Figure (3), it is measured the liquid transit time from line 1 to line 2. The measurement was started with solvent (Toluene) first, then flow times of five different concentrations of polymer solution were recorded as shown in Figure (4). Each test was repeated at least twice for more accuracy.



Figure (4): Five different concentrations of the polymer solution.

The corrected average flow time t_i (correction) for a solvent (t_0) and each polymer concentration, was calculated by subtracting the Hagenbach correction (ψ) from the average flow time (t_i) for that concentration according to [8]:

$$t_i ext{ (correction)} = t_i - \psi ext{ (1)}$$

where: ψ is a correction factor termed "Hagenbach correction" which is added to allow for the effects of the kinetic energy of efflux. The Hagenbach correction can be estimated according to the relation [8]:

$$(2) \times \quad \psi = (B/(c))$$

where: B is a constant related to the dimensions of the viscometer and c is viscometer constant. The Hagenbach correction was provided in the operating instruction for the viscometer. For each polymer concentration, the following viscosities were determined using the Equation given [9]:

Relative viscosity,
$$\eta_{\text{rel}} = (t_i/t_0)$$
 (3)

Specific viscosity,
$$\eta_{sp} = (t_i/t_0) - 1$$
 (4)

Reduced viscosity,
$$\eta_{red} = (\eta_{sp}/C)$$
 (5)

Inherent viscosity,
$$\eta_{inh} = (\ln \eta_{red} / C)$$
 (6)

The reduced viscosity and inherent viscosity were plotted against polymer concentration (C), as shown in Figure (5). The value of intrinsic viscosity can be calculated by extrapolating graph of reduced viscosity and inherent viscosity to zero concentration. The average of the two obtained intercept values was calculated [9].

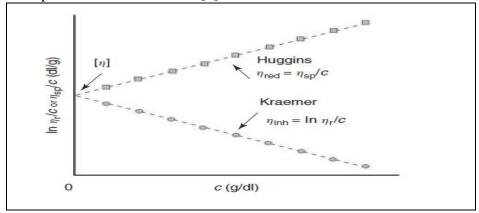


Figure (5): The Kraemer–Huggins plot to obtain the intrinsic viscosity, where the inherent viscosity is defined as $\eta_{inh} = \ln \eta_r / C$ [9].

B- Average Molecular Weight Determination

Viscosity-average molecular weight was identified by viscometric measurements using an Ostwald Capillary Viscometer. This value was calculated from Mark-Houwink-Sakurada Equation [5]:

$$(7) \overline{M} v \times [\eta] = (K)$$

where: $[\eta]$ = intrinsic viscosity, $\overline{M}v$ = viscosity average molecular weight, K and α are constants for a given polymer-solvent-temperature system.

4- Result and Discussion

The intrinsic viscosity for determination of the molecular weight of the polymer is calculated.

- The Viscosity of the solvent (toluene) is measured using a viscosity device (Viscometer).
- Using the flow time (t), the reduced viscosity (η_{red}) is calculated at different concentrations using Equation (8)[9] as shown in Table (1).

$$\eta_{\text{red}} = \left[\left(t - t_0 \right) / \left(C \times t_0 \right) \right] \tag{8}$$

where: η_{red} = reduced viscosity, t_0 = average flow time for solvent, t = average flow time for various polymer solution concentration. C = the polymer solution concentration.

Table (1): Experimental data and results of reduced viscosity for PS and PDMS.

| Concentration | PS | | PDMS | |
|---------------|------------|---|----------|--|
| C (g/ml) | Time | Reduced viscosity | Time (s) | Reduced viscosity |
| | (s) | 10 ⁻² ×η _{red} (ml/g) | | $10^{\text{-}2} \times \eta_{red} \; (ml/g)$ |
| 0 | 97 | - | 97 | - |
| 0.002 | 107 | 0.5155 | 106 | 0.4639 |
| 0.004 | 118 | 0.5412 | 117 | 0.5155 |
| 0.006 | 132 | 0.6014 | 133 | 0.6186 |
| 0.008 | 151 | 0.6959 | 149 | 0.6701 |
| 0.01 | 166 | 0.7113 | 168 | 0.7320 |

 Reduced viscosity (η_{red}) is plotted with solution concentration (C). The intercept point of the straight line with the y-axis determines the intrinsic viscosity at C equal 0. From Figures (6) and (7) for PS and PDMS respectively.

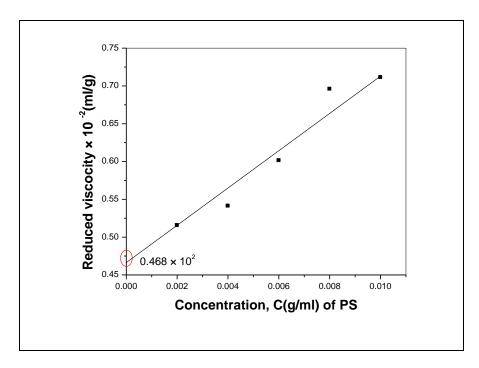


Figure (6): Plot of reduced viscosity, η_{red} (ml/g) against concentration, C (g/ml) of PS.

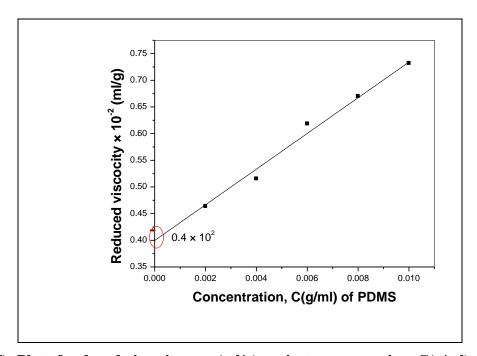


Figure (7): Plot of reduced viscosity, η_{red} (ml/g) against concentration, C(g/ml) of PDMS.

• This value of intrinsic viscosity is used to calculate the molecular weight from Equation (7) [5] as shown in Table (2).

Table (2): Solvent data and results of intrinsic viscosity and molecular weight of (PS) and (PDMS).

| Solvent data toluene at (25°C) | Polystyrene (PS) | Polydimethylsiloxane (PDMS) | Reference |
|---|-----------------------|--------------------------------|-----------|
| K (cm³/g) | 0.85×10^{-2} | 20 × 10 ⁻³ | [6] |
| α | 0.75 | 0.66 | [6] |
| Intrinsic viscosity, η (ml/g) | 0.468×10^{2} | 0.4×10^{2} | - |
| Average molecular weight, ${M_V}$ (g/mol) | 97,223.05 | 100,359.98 | <u>-</u> |

The accuracy of determining the viscosity average molecular weight op (PS) and (PDMS) depends on several factors, including the polymers nature, the solvent used, and the temperature.

4.1 Effect of Polymer Structure on Calculated Molecular Weight

It is observed that (PS) has a lower molecular weight compared to (PDMS), which can be attributed to the differences in their polymer structures. Polymer with aromatic side chains, leading to strong interactions with the solvent and a significant effect on intrinsic viscosity. On the other hand, (PDMS) is a flexible polymer with silicon-oxygen linkages, which grants it relatively low viscosity.

4.2 Effect of Solvent on the Results

The calculations were carried out using toluene as solvent, which is a good solvent for both (PS) and (PDMS), but it affects them differently in terms of chain relaxation in the solution. For (PS), toluene causes swelling of the polymer chains, leading to higher intrinsic viscosity and consequently, a high molecular weight. In contrast, for (PDMS), toluene does not cause the same degree of chain extension, leading to lower intrinsic viscosity and a higher molecular weight estimate.

4.3 Accuracy and Limitations of the Viscosity Method

Although the viscosity method provides a good estimation of molecular weight, it has some limitations, including:

- It relies on **Mark Houwink constants**, which can vary depending on the experimental conditions.
- It does not provide information on molecular weight distribution, only giving an average molecular weight value.

• The method is sensitive to concentration and solvent, which can lead to discrepancies under different conditions.

4.4 Comparison with Other Methods

The results obtained from the viscosity method can be compared with other techniques, such as Gel Permeation Chromatography (GPC), which provides more precise information rather than just an average value, as with viscosity. Therefore, combining both methods could offer a clearer picture of the polymers molecular weight.

5- Conclusion

Determining the molecular weight of polymers such as (PS) and (PDMS) is essential for understanding their physical properties and applications. The viscosity method is based on the Mark-Houwink equation, which relates the intrinsic viscosity of a polymer solution to its molecular weight using experimentally determined constants specific to each polymer-solvent system. Our calculations showed that the viscosity average molecular weight of (PS) in toluene at 25°C is approximately (97,223.05 g/mol) while for (PDMS) under the same conditions, it is (100,359.98 g/mol). This difference highlights the influence of polymer structure and solvent interactions on intrinsic viscosity, which affects molecular weight estimation. Furthermore, it was concluded that the intrinsic viscosity and viscosity-average molecular weight of the polymer can be determined using an Ostwald Viscometer. The viscosity method is a practical and efficient approach for estimating polymer molecular weight, however, its accuracy depends on the availability of precise Mark-Houwink constant. To gain a more comprehensive understanding of molecular weight distribution, it is recommended to complement this method with techniques such as Gel Permeation Chromatography (GPC) for more precise and detailed measurements.

References:

- [1] Goddard, E. D., Ananthapadmanabhan, K. (1993), Interactions of Surfactants with Polymers and Proteins; CRC Press, Boca Raton.
- [2] Narain, R. (2020). Polymer Science and Nanotechnology: Fundamentals and Applications. 1st ed. Elsevier.
- [3] Toms, B.A., Some Observations on The Flow of Linear Polymer Solutions through Straight Tubes at Large Reynolds numbers, Proc. 1st Intern. Congr. Rheol., Vol.2, pp 135-141, North Holland, (1948).
- [4] Truong, V. T. (2002), Drag Reduction Technologies. http://www.dsto.defence.gov.au/corporate/reports/DSTO-GD-0290.pdf.
- [5] Barth, H. G., Mays. J. W. (1991), Modern Methods of Polymer Characterization.1st ed., New York: Wiley, PP. 2321.
- [6] Brandrup, J. Immergut, E. H. and Grulke, E. A. (1999), Polymer Handbook. 4th ed. New York: Wiley.
- [7] Taylor and Francis Group (2006), Introduction to Polymer Science and Chemistry. Boca Raton New York.
- [8] Brown, R. P. (1981), Handbook of Plastics Test Methods. 2nd edition, George Godwin Ltd: London.
- [9] Appletion, J. D. Hooker, P. J. and Smith, N. J. P. (1995), Report on the abatement of volatile organic compounds from stationary sources. Report to the department of the environment, London. contract no. PECD 7/12/138.

.