International Journal of Advanced Technology in Engineering and Science
Vol. No.5, Issue No. 07, July 2017
www.ijates.com
ijates
ISSN 2348 - 7550

Determination of MWD of a Polymer Sample by Viscometric Measurements of Polymer Solution.

Dr. Aniruddh Singh

Dept. Of Applied Science and Humanities, Ajay Kumar Garg Engineering College, APJ AKTU
Ghaziabad, U.P.,(India)

ABSTRACT

The molecular weight distribution (mwd) characterization of polymers is routinely conducted in solution by Gel Permeation Chromatography. The method however has some limitations. The GPC can resolve limited no. of peaks within a short time scale of GPC run. Also the method does not give satisfactory results in high and ultralow molecular weight range. In this article I propose an alternative method to extract the mwd and the polydispersity index of a polymer sample by viscometric analysis of dilute solution of the given sample. The advantage of this method is that it can be applied to multimodal distributions and can resolve large no. of peaks and is applicable for all molecular weights. The method is also cheaper and can be performed in a usual undergraduate laboratory.

Keywords: Molecular Weight Distribution, Polymer, Viscosity.

I. INTRODUCTION

The molecular weight distribution is an important physical criteria which deeply influence the end use properties of a polymer. The average molecular weight is tuned to a desired value to obtain the required properties. But often the control on the average molecular weight is inadequate and one needs control over the entire molecular weight distribution to get the desired result. The polydispersity index is a measure of the breadth of the polymer mwd but is an in sufficient parameterization for complicated mwds. Sometimes the same value of PDI for two different samples have entirely different properties. In certain situations, it is often desired to control the amount of polymers in certain molecular weight ranges [1]. Thus properties like tensile strength , impact resistance and hardness the finished product are closely related to the mwd of the constituent polymer material.

Viscometry is considered to be a reliable method to determine average molecular mass of a polymer when dispersity data is not needed. The governing equation which relates the limiting viscosity $[\eta]$ with the viscosity averaged molecular mass is known as the Mark- Houwink-Sakurada (MHS) equation:

$$[\eta] = k\overline{M}_V^{a}$$

where k and a are constants for a given well-defined polymer-solvent-temperature system.

To get the mwd it is generally resorted to the standard method of Size Exclusion Chromatography (SEC) or Gel Permeation Chromatography (GPC). SEC provides information on the molar mass distribution but it is not an easy technique for aromatic polyesters due to their poor solubility in commonly used SEC eluents .In other cases the refractive indexes of the polymer and the solvent are very close to each other (dn/dc ~ 5·10–2 mL·g–1) so inaccuracies are observed. This is one of the reasons why the determination of molar mass by SEC with a refractive index or light scattering detector for some polymers is controversial in some specific solvents and errors estimated in such cases is close to 50% [2].

The objective of the presented work is to develop a novel technique to extract the mwd from viscometric data alone. As is recognized viscometry is one of the simplest technique for polymer characterization and is most easily accessible. In this work the usual 2-dimentional viscometric data (kinematic viscosity versus concentration) is extended in the third dimension viz. temperature or polymer solvent system. With the extension of data points it becomes possible to extract the standard deviation of the normal distribution which is introduced to model the real time mwd of the polymer sample.

II.EXPERIMENTAL AND CALCULATIONS

A solution of 1 gm in 100 ml of polystyrene in benzene was taken. An Ubbelohde viscometer with capillary diameter 0.63 mm was purchased from SI Analytics ,Germany and SI Analytic automatic viscosity measurement comprising of Xylem Analytic Viscoclock to measure the flow time with an accuracy of 0.1% was also purchased. The solution viscosity was measured for four different concentration starting from 1gm in 100 ml to 0.2 gm in 100ml. The viscosity of pure benzene was also measured. These measurements were taken at two different temperature viz: 30^{o}C and 25^{o}C. To maintain temperature the viscometer was kept in a Siskin Viscobath with a stability of $\pm 0.01^o$C. The intrinsic viscosity was calculated by using Huggins and Kramer equations:

$$\eta_{rel} = \frac{t}{t_o} \qquad (1)$$

$$\eta_{sp} = \frac{t - t_o}{t_o} \qquad (2)$$

$$[\eta] - k_1[\eta]^2 C = \frac{\eta_{sp}}{C} \quad \text{(Huggins)} \qquad (3)$$

$$[\eta] - k_2[\eta]^2 C = \frac{\ln \eta_{rel}}{C} \quad \text{(Kramer)} \qquad (4)$$

where k1 and k2 are the Huggins and Kramer coefficients, respectively and C is the concentration of the polymer solution in g/ml . For each sample η_{sp}/C and $(\ln \eta_{rel})/C$ were plotted against the concentration C (Huggins and Kramer plots) and the intrinsic viscosity was obtained by extrapolating the plots to infinite dilution[3]. The respective graph for 30^{o}C and 25^{o}C are shown below.

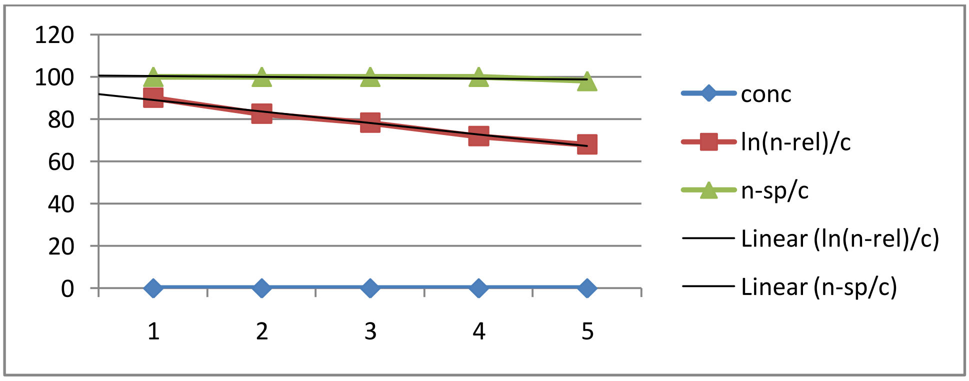

Fig.1 Reduced and inherent viscosity –concentration curve for polystyrene in benzene at 30^{o}C

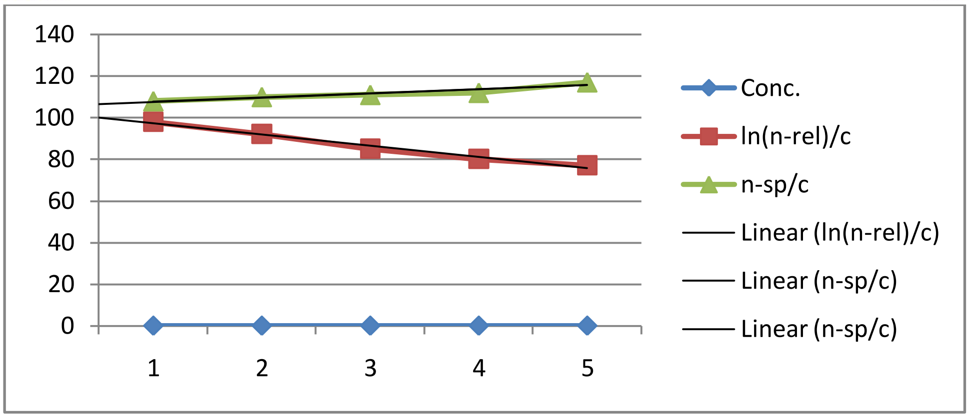

Fig.2 Reduced and inherent viscosity –concentration curve for polystyrene in benzene at 25°C

III. CALCULATION AND RESULT

The result of the experimentation on polystyrene in benzene is tabulated in the following table:

Polystyrene in Benzene	At 30°C $[\eta_1]$	At 25°C $[\eta_2]$
Intrinsic viscosity $[\eta]$	100 ml/gm	110 ml/gm

The viscosity averaged molecular mass is defined as:

$$\overline{M}_V = \frac{\int_0^\infty F(\overline{M},\sigma) M^{1+a}\, dM}{\int_0^\infty F(\overline{M},\sigma) M\, dM} \qquad (5)$$

Where F is the appropriate mwd with mean $\overline{M}$ and breadth σ.

We model the given distribution by a normal distribution of unknown mean and breadth:

$$F(\overline{M},\sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(\frac{-(M-\overline{M})^2}{2\sigma^2}\right) \qquad (6)$$

Then according to Mark Houwink Sakurada equation:

$$[\eta] = k\left(\frac{\int_{-\infty}^{\infty} F(\overline{M},\sigma) M^{1+a}\, dM}{\int_{-\infty}^{\infty} F(\overline{M},\sigma) M\, dM}\right) \qquad (7)$$

Where we have changed the limits of integration from (0 to infinity) to (–infinity to +infinity) as negative values of x are not allowed as the molecular mass of a single chain cannot be negative.

From the above table:

$$\frac{[\eta_1]}{[\eta_2]} = \frac{k_1}{k_2}\frac{\int_{-\infty}^{+\infty} F(\overline{M},\sigma) M^{1+a_1} dM}{\int_{-\infty}^{+\infty} F(\overline{M},\sigma) M^{1+a_2} dM} \qquad (8)$$

Where k_1, a_1 are the value of the MHS constants at 30$^{\mathrm{o}}$C and k_2, a_2 at 25$^{\mathrm{o}}$C.

Now consider the integral: $\int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-\frac{(M-\overline{M})^2}{2\sigma^2}) M^{1+a} dM$

It can be rewritten by change of variable $x = (M - \overline{M})/\sqrt{2}\sigma$

$$= \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-x^2)(\sqrt{2}\sigma x + \overline{M})^{1+a}\sqrt{2}\sigma dx \qquad (9)$$

Which on further rearrangement gives:

$$= \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-x^2)(\sqrt{2}\sigma)^{1+a}(x + \frac{\overline{M}}{\sqrt{2}\sigma})^{1+a}\sqrt{2}\sigma dx \qquad (10)$$

$$= \frac{2\sigma^{2+a}}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} \exp(-x^2)(x + \overline{Y})^{1+a} dx \qquad (11)$$

With $\overline{Y} = \frac{\overline{M}}{\sqrt{2}\sigma}$

Pulling out $\overline{Y}$ we get:

$$= \frac{2\sigma^{2+a}}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} \exp(-x^2)(\overline{Y})^{1+a}(1 + \frac{x}{\overline{Y}})^{1+a} dx \qquad (12)$$

Since the normal distribution in the integral above had a standard deviation of the order one therefore vanishes before x approaches $\overline{Y}$, in general $|x| << \overline{Y}$ .Therefore one can Maclaurin expand up to second order.:

$$= \frac{2\sigma^{2+a}}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} \exp(-x^2)(\overline{Y})^{1+a}(1 + (1+a)\frac{x}{\overline{Y}} + \frac{a(a+1)}{2}\left(\frac{x}{\overline{Y}}\right)^2)\ dx \qquad (13)$$

Now it is possible to integrate:

$$= \frac{2\sigma^{2+a}}{\sqrt{2\pi\sigma^2}} \left(\frac{\overline{M}}{\sqrt{2}\sigma}\right)^{1+a} [\frac{\sqrt{\pi}}{1} + \frac{a(a+1)}{2\overline{Y}^2}\frac{\sqrt{\pi}}{2}] \qquad (14)$$

Equation (7) then becomes:

$$[\eta] = \frac{k 2\sigma^{2+a}}{\sqrt{2\pi\sigma^2}} \left(\frac{\overline{M}}{\sqrt{2}\sigma}\right)^{1+a} \frac{1}{\overline{M}} [\frac{\sqrt{\pi}}{1} + \frac{a(a+1)}{2\overline{Y}^2}\frac{\sqrt{\pi}}{2}] \qquad (15)$$

$$= k\overline{M}^{a}[1+\frac{a(a+1)}{4\overline{Y}^{2}}] \quad (16)$$

Taking the log of equation (15)

$$\ln[\eta] = \ln k + a\ln\overline{M} + \ln[1+\frac{a(a+1)}{\overline{Y}^{2}}] \quad (17)$$

On further expansion of ln(1+x) upto first order:

$$\ln[\eta] = \ln k + a\ln\overline{M} + \frac{a(a+1)}{\overline{Y}^{2}} \quad (18)$$

The above equation will result in two equations one for each temperature. The system of two equations can be solved for two unknowns, $\overline{M} and \overline{Y}$.

Below we tabulate the values of MHS constants of Polystyrene in Benzene at two temperatures:

MHS constants	30^{o}C[4]	25^{o}C[4]
k (ml/g)	1.623×10^{-2}	1.13×10^{-2}
a	0.695	0.73

Plugging in the numbers we get:

$\overline{M} = 88787.39$, $\overline{M_v} = 283594.30$ and $\sigma = 36780.19$.

IV. CONCLUSION

It has been shown in this paper that viscometric measurements can determine the value of the breadth of the molecular weight distribution along with the usual estimate of the viscosity averaged molecular weight. The number average molecular weight can also be calculated from the above method and a succinct expression relating the number averaged molecular weight and viscosity averaged molecular weight is derived.

V.ACKNOWLEDGEMENT

I thank Dr. R.K. Agarwal, Director ,Ajay Kumar Garg Engieering College and Prof. S.L. Kapoor, HOD, Applied Science, AKGEC, for giving me opportunity to conduct research in college and providing me amenities for the same.

REFERENCES

[1] Bersted, B. H.; Anderson, T. G. *Influence of Molecular Weight and Molecular Weight Distribution on the Tensile Properties of Amorphous Polymers. J. Appl. Polym. Sci. 1990, 39, 499*

[2] Q. Charlier, E. Girard, F. Freyermouth, M. Vandesteene, N. Jacquel, C. Ladavière, A. Rousseau, F. Fenouillot. *Solution viscosity – molar mass relationships for poly(butylene succinate) and discussion on molar mass analysis. eXPRESS Polymer Letters Vol.9, No.5 (2015) 424–434.*

[3] F.W. Billmeyer, *Textbook of Polymer Science, Wiley Edition, page 209-210.*

[4] Appendix I **-** Springer Link ***link.springer.com/content/pdf/bbm%3A978-3-662-03910-6%2F1.pdf***