Korea Polymer Journal, Vol. 8, No. 5, pp 243 – 245 (2000)

Notes

Determination of Viscosity Average Molecular Weight from Number and Weight Average Molecular Weights

Eun-Soo Park and Jin-San Yoon*

Department of Polymer Science and Engineering Inha University, Inchon 402-751, Korea

Received June 22, 2000

Abstract : A theoretical equation for the viscosity average molecular weight is derived as $\overline{M}_v = \{(1/y^a)(\Gamma(z+a+1)/(\Gamma(z+1))\}^{1/a}(M_0)$, where the adjustable parameters, y and z, of the Schultz-Zimm distribution can be determined from the number and weight average molecular weights. When the value of the exponent, a, appearing in the relation between the intrinsic viscosity and the viscosity average molecular weight, is in the range from 0.6 to 0.8, as is the case for the most polymers, the viscosity average molecular weight is much more close to the weight average molecular weight than to the number average molecular weight.

Introduction

The number and weight average degrees of polymerization can be determined theoretically from polymerization mechanism and kinetics when reaction rate constants of the elementary reactions are constant as is the case with polymerizations in continuous stirred tank reactors. However, many industries use the viscosity average molecular weight in place of the number and weight average molecular weights for their product control.

In this study, a theoretical equation is derived to correlate the viscosity average molecular weight with the number and weight average molecular weights when the molecular weight distribution of the polymers follows the Schultz-Zimm distribution.

Theoretical Equations

The average intrinsic viscosity is given as a function of viscosity average molecular weight as Eq(1).[1]

$$\overline{[\eta]} = K\overline{M}_v^{\,a} \tag{1}$$

For a molecule whose molecular weight is M_i, the intrinsic viscosity is expressed as Eq(2),[1] and the average intrinsic viscosity becomes as in Eq(3)[2]

$$[\eta]_i = KM_i^a \tag{2}$$

$$\overline{[\eta]} = w_i\,[\eta_i] = K\sum w_i M_i^{\,a} \tag{3}$$

Therefore, viscosity average molecular weight yields to be Eq(4).

$$\overline{M}_v = \left\{\sum w_i M_i^{\,a}\right\}^{1/a} = \left\{\sum (i^a w_i)\right\}^{1/a} M_0 \tag{4}$$

where w_i is weight fraction of molecules whose degree of polymerization is i, and M_0 is average molecular weight of the structural unit constituting the polymer molecule.

Because the weight fraction w_i can be expressed as Eq(5), the rearrangement of Eq(4) yields Eq(6)

$$w_i = \frac{iP_i}{\sum iP_i} \tag{5}$$

$$\overline{M}_v = \left\{\frac{\sum i^{a+1}P_i}{\sum iP_i}\right\}^{\frac{1}{a}} M_0 \tag{6}$$

---

*e-mail : jsyoon@inha.ac.kr

where P_i is the concentration of polymer molecules whose degree of polymerization is i.

The Schultz-Zimm distribution function for weight fraction, w_i, and for number fraction, n_i, can be written as Eq(7) and (8).[3]

$$w_i = \frac{y^{z+1}}{\Gamma(z+1)} i^z e^{-yi} \tag{7}$$

$$n_i = \frac{y^z}{\Gamma(z)} i^{z-1} e^{-yi} \tag{8}$$

Therefore, the weight-average and number-average degree of polymerization μ_w and μ_n, can be derived to be as Eq(9) and (10).[2]

$$\mu_w = \int_0^\infty i w_i di = \frac{z+1}{y} \tag{9}$$

$$\mu_n = \int_0^\infty i n_i di = \frac{z}{y} \tag{10}$$

where both z and y can be determined from μ_w and μ_n.

From Eq(4) and (7) the viscosity-average degree of polymerization, μ_v can be shown as

$$\mu_v = \left\{ \frac{y^{z+1}}{\Gamma(z+1)} \int_0^\infty i^{z+a} e^{-yi} di \right\}^{\frac{1}{a}} \tag{11}$$

Hence, μ_v and $\overline{M}_v$ can be calculated by Eq(12) and Eq(13), respectively, from the adjustable parameters, y and z, of the Schulz-Zimm distribution function.

$$\mu_v = \left\{ \frac{1}{y^a} \frac{\Gamma(z+a+1)}{\Gamma(z+1)} \right\}^{\frac{1}{a}} \tag*{(12)^4}$$

$$\overline{M}_v = \mu_v M_0 \tag{13}$$

Discussion

Randomly coiled polymers have the value of the exponent, a, in the range between 0.5 and 1.0.

Figure 1 shows μ_v as a function of a for μ_n = 1,000 and μ_w = 2,000. When a is equal to -1.0, μ_v is equal to μ_n. As a approaches to 1.0, μ_v increases almost linearly to μ_w. Since most polymers have their a values between 0.6 and 0.8, μ_v is more inclined to μ_w than to μ_n.

Figure 2 demonstrates the variation of μ_v/μ_w as

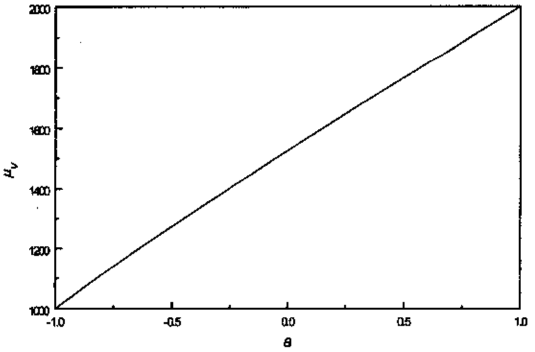

Figure 1. μ_v as a function of the exponent a for a polymer whose μ_n and μ_w are 1,000 and 2,000, respectively.

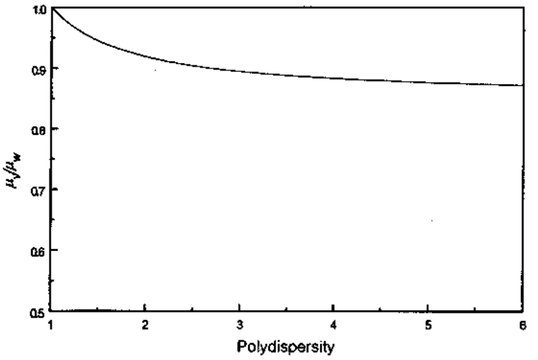

Figure 2. Variation of μ_v/μ_w as a function of the polydispersity, μ_w/μ_n. The value of the exponent, a, was fixed at 0.65. The curves for different values of μ_w overlapped completely with each other.

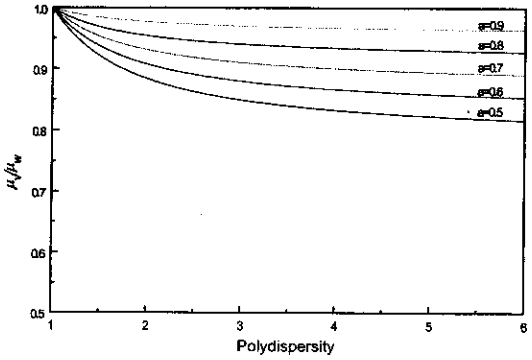

Figure 3. Dependence of μ_v/μ_w on μ_w/μ_n the polydispersity index at different values of the exponent, a.

a function of μ_w/μ_n, the polydispersity index, at a fixed value of a. The curves for different values of μ_w, overlap with each other completely, indicating that dependence of the ratio, μ_v/μ_w, on the polydispersity index is independent of the value of μ_w.

Dependence of μ_v/μ_w on the polydispersity index at different values of a is shown in Figure 3. μ_v deviates from μ_w as the polydispersity index is increased. However, it can be perceived that μ_v is not too much smaller than μ_w for most polymers.

Acknowledgement. This work was supported by grant No. 1999-2-308-004-3 from the interdisciplinary research program of the KOSEF.

References

(1) M. Kurata, Y. Tsunashima, M. Iwama, and K. Kamada, *Polymer Handbook,* J. Brandrup and E. H. Immergut, Eds., John Wiley and Sons, New York, 1975, Ch. 4.

(2) F. W. Billmeyer, *Text book of Polymer Science,* 3rd Ed., John Wiley and Sons, New York, 1984, Ch. 8.

(3) B. H. Zimm, *J. Chem. Phys.,* **16**, 1099 (1948).

(4) A computer program is available upon request for calculation of the gamma function.