

**Comment on the Novel Parameter of Polymer Structure
Suggested by W. S. Bahary**

With the aim of finding a simple and reliable method for the determination of the breadth of molecular weight distributions of high molecular weight compounds, W. S. Bahary¹ proposed the measurement of the ratio of concentrated solution viscosities η_s and the limiting viscosity number $[\eta]$:

$$\eta_s/[\eta] = \text{ROV}$$

This approach is based on the fact that these two quantities are functions of different molecular weight averages, namely \bar{M}_w and \bar{M}_η , respectively:

$$\eta_s = K_1 w_1 (\bar{M}_w)_{M < M_{cr}} + K_2 w_2^{3.5} (\bar{M}_w)_{M > M_{cr}}^{3.5} \quad (1)$$

$$[\eta] = K_3 \bar{M}_\eta^\alpha \quad (2)$$

$(\bar{M}_w)_{M \leq M_{cr}}$ means the weight-average molecular weights of all polymers below or above the critical molecular weight M_{cr} ; the relative weights of these two portions are w_1 and w_2 , respectively. \bar{M}_η is the viscosity-average molecular weight, defined by

$$\bar{M}_\eta = (\sum w_i M_i^\alpha)^{1/\alpha}$$

w_i being the weight fraction of the i th component, while K_1 , K_2 , and K_3 normally are constants for a given temperature and polymer-solvent system.

One of the main difficulties for more than qualitative comparability of ROV values lies in the fact, that eq. (1) is only a special case of eq. (3) which states that the concentrated solution viscosities depend on polymer concentration c times density ρ to the power of α and on M to the power of β , α and β varying with chain length.²

$$\eta_s = k(c\rho)^\alpha M^\beta \quad (3)$$

If, however, for the moment we assume the existence of two molecular weight ranges of constant α and β as proposed in eq. (1), a discussion of the ratio of η_s and $[\eta]$ as a means for the determination of heterogeneity indices is possible.

Apart from a few trivial assumptions Bahary postulates, first, that the polymer should contain some molecules having a molecular weight greater than the critical value and, second, that the range of intrinsic viscosities to be compared should be narrow.

For the general case with finite amounts of polymers on both sides of M_{cr} , ROV becomes

$$\text{ROV} = \frac{K_1 w_1 (\bar{M}_w)_{M < M_{cr}} + K_2 w_2^{3.5} (\bar{M}_w)_{M > M_{cr}}^{3.5}}{K_3 \bar{M}_\eta^\alpha} \quad (4)$$

and it is readily seen that, for constant $[\eta]$, the greater the product of $w_2 (\bar{M}_w)_{M > M_{cr}}$, the larger the value of ROV, subject to the condition that K_1 and K_2 are of the same order of magnitude.

If, however, for easier discussion we examine the validity of ROV for the special case of polymers containing only homologs either below or above M_{cr} , eq. (4) reduces to

$$\eta_s/[\eta] = (K_1/K_3) (\bar{M}_w/\bar{M}_\eta)^\alpha \bar{M}_w^{-\alpha} \quad \text{All } M < M_{cr} \quad (4a)$$

$$\eta_s/[\eta] = (K_2/K_3) (\bar{M}_w/\bar{M}_\eta)^\alpha \bar{M}_w^{3.5-\alpha} \quad \text{All } M > M_{cr} \quad (4b)$$

In both cases ROV is not only a function of the ratios of two different molecular weight averages, but also of the absolute weight-average molecular weight. This is the reason, why Bahary¹ was forced to confine the application of his novel parameter to samples lying within a narrow range of intrinsic viscosities.

If $[\eta]$ and therefore \bar{M}_η is kept constant, η_s , which depends on \bar{M}_w or $\bar{M}_w^{3.5}$, respectively, will reflect the high molecular weight ends of the molecular weight distribution,

since the contribution of a certain amount of a certain polymer homolog to \bar{M}_w exceeds the contribution to \bar{M}_η , the more the higher the molecular weight and the lower the value of α .

If, in the light of the above discussion, we now examine the experimental data given by Bahary, we see that the intrinsic viscosities of his milled products 110, 115, and 116 lie within the range of 10%, likewise therefore \bar{M}_η^α . The ratio of his measured ROV values of these three samples are:

$$\text{ROV}_{110} : \text{ROV}_{115} : \text{ROV}_{116} = 1.00 : 1.05 : 1.58$$

For the \bar{M}_w values given by Bahary,¹ eq. (4a) yields for the above sequence of samples 1.0:2.8:9.2, whereas eq. (4b) yields 1:37:3020. The agreement with the measured ROV values is poor for eq. (4a), but even worse for eq. (4b). And it is really the latter equation which should be applied here, since the results of Bahary imply that all molecular weights of the above-mentioned products are greater than the critical value.

The poor agreement may be attributable partly to incorrect \bar{M}_w values as a consequence of microgel still present or/and incorrect η_s values not extrapolated to zero velocity gradient, perhaps also to the inapplicability of eq. (1).

The above discussion shows, that Bahary's "novel parameter" of polymer structure, ROV, unfortunately, is of no general value, since it does not yield directly comparable values for a number of reasons. Its usefulness is therefore restricted to samples having either equal \bar{M}_w values or equal intrinsic viscosities.

The concentrated solution viscosities at constant $[\eta]$ might be of some help in indicating high molecular weight ends in molecular weight distribution, although until now quantitative agreement between experiment and theory could not be achieved, as was demonstrated for the above data.

References

1. W. S. Bahary, *J. Appl. Polymer Sci.*, **10**, 473 (1966).
2. S. Onogi, S. Kimura, T. Kato, R. Masuda, and N. Miyanaga, in *U.S.-Japan Seminar in Polymer Physics (J. Polymer Sci. C, 15)*, R. S. Stein and S. Onogi, Eds., Interscience, New York, 1966, p. 381.

B. A. WOLF

Institut für Physikalische Chemie
Universität Wien
Vienna, Austria

Received June 26, 1967

Revised October 2, 1967