(5) Although crystallite sizes, size distributions and paracrystalline lattice distortions remain constant, the d.t.a. curve shifts to higher temperatures and becomes sharper on annealing. This can be explained only by assuming that the average surface free energy $\overline{\sigma'_e}$ decreases and that the distribution of the (σ'_e/D_{012}) values narrows on annealing.

(6) The melting process starts preferentially at locations, where lamellae end, thus creating unprotected lateral and fold surfaces with high σ'_e values. This confirms the published[11] mechanism of increasing long period and lamellae thickness during annealing and heating.

ACKNOWLEDGEMENTS

Thanks are due to Dr G. Goldbach (Chemische Werke Hüls) for supplying the samples of poly(1- butene).

REFERENCES

1 Rubin, I. R. *J. Polym. Sci. (B)* 1964, **2**, 747

2 Haase, J., Hosemann, R. and Renwanz, B. *Colloid Polym. Sci.* 1977, **255**, 849

3 Hoffman, J. D. in 'Treatise on Solid State Chemistry', Plenum Press, 1976, Vol 3

4 Wilski, H. and Grewer, T. *J. Polym. Sci. (C)* 1964, **6**, 33

5 Sanchez, I. R. and Eby, R. K. *J. Res. Nat. Bur. Stand, (A)* 1973, **77**, 774

6 Hosemann, R. and Bagchi, S. N. in 'Direct Analysis of Diffraction by Matter' North-Holland, Amsterdam, 1962

7 Kilian, H. G. *Kolloid Z. Z. Polym.* 1969, **231**, 534

8 Fischer, E. W. *Kolloid Z. Z. Polym.* 1969, **231**, 458

9 Overbergh, N., Berghmans, H. and Reynaers, H. *J. Polym. Sci.* 1976. **14**, 1177

10 Petermann, J., Miles, M. and Gleiter, H. *J. Macromol. Sci. (B)* 1976, **12**, 393

11 Hosemann, R. *Polymer* 1962, **3**, 349

An improved graphical method for the evaluation of molecular weight measurements on polymers

T. T. Nagy, T. Kelen and F. Tüdös

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

(Received 4 April 1978; revised 13 June 1978)

We have previously suggested a new linear graphical method with several advantages for the determination of copolymerization constants[1]. By this method, the straight line:

$$y = ax + b \qquad (1)$$

with introduction of the new variables

$$f = \frac{x}{\gamma + x} \text{ and } g = \frac{y}{\gamma + x} \qquad (2)$$

is transformed into the straight line

$$g = a'f + b' \qquad (3)$$

by the application of which the parameters

$$a = a' + b' \quad \text{and} \quad b = b'\gamma \qquad (4)$$

can be determined from the data points with better reliability than by the application of the original equation (1).

In the above relations, γ is an appropriately chosen constant. In copolymerization systems, the most feasible procedure proved to be[2–5] to choose the γ value so as to obtain experimental points in the most extended and at the same time most symmetrical arrangement; then from the determining equation:

$$f_m = 1 - f_M \qquad (5)$$

we have

$$\gamma = \sqrt{x_m x_M} \qquad (6)$$

(where the lowest f and x values are denoted by f_m and x_m and the highest by f_M and x_M, respectively).

Our choice of the auxiliary parameter, γ may be governed, however, by other principles as well, e.g. by the requirement of obtaining a more uniform error distribution by the transformation, in order to increase the reliability of evaluation. This is possible if the standard deviation of measurement can be given in a simple form, e.g. as an explicit function of the independent variable. In such a case, for the determining equation we have:

$$\sigma(g_m) = \sigma(g_M) \qquad (7)$$

i.e. the γ value must be chosen so that the transformation yields identical standard deviations (σ) for data measured at the lowest and highest indepentdent variables.

In this Note we deal with the specific, though not unique case when the standard deviation of the data is inversely proportional to the value of the independent variable. This is the case for osmometric and viscometric molecular weight determinations when (π/c) *versus* (η_{sp}/c) data are extrapolated to zero concentration. The standard deviations of the osmotic pressure $\sigma(\pi)$ and of the specific viscosity $\sigma(\eta_{sp})$ are nearly constant. Using the symbols $y = \pi/c$ vs. η_{sp}/c and $x = c$ as in equation (1), we have $\sigma(y) = \sigma(\pi)/x$ vs. $\sigma(\eta_{sp})/x$ and $\sigma(y)$ is inversely proportional to x: $\sigma(y) \approx 1/x$. According to this treatment:

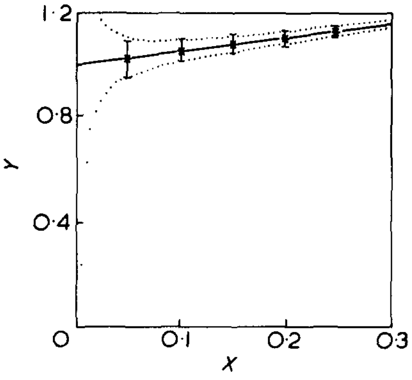

Figure 1 Measured $y = \eta_{sp}/c$ values as a function of $x = c$ concentration. The stars denote the average of 30 measurements. Broken lines are calculated scatter curves

$$\sigma(g) = \frac{\sigma(y)}{\gamma + x} \approx \frac{1/x}{\gamma + x} \qquad (8)$$

in other words, the determining equation (7) of γ auxilliary parameter is then:

$$\frac{1/x_m}{\gamma + x_m} = \frac{1/x_M}{\gamma + x_M} \qquad (9)$$

0032-3861/78/111360-02$02.00

Table 1 Viscosity measurement on PVC solutions

$x = c$ (g/dl)	$\bar{t}$ (sec)	$y = \eta_{sp}/c$ $(g/dl)^{-1}$	F	G $(g/dl)^{-2}$
0	36.903	–	–	–
0.05	38.792	1.023	0.2	4.09
0.10	40.810	1.058	0.5	5.29
0.15	42.910	1.085	1.0	7.23
0.20	45.038	1.102	2.0	11.02
0.25	47.352	1.132	5.0	22.64

Table 2 Average and standard deviation of intrinsic viscosity and slope, calculated from 30 measurements

	$[\eta]$ $(g/dl)^{-1}$	$\sigma([\eta]$ $(g/dl)^{-1}$	a $(g/dl)^{-2}$	$\sigma(a)$ $(g/dl)^{-2}$
Based on diagram η_{sp}/c vs. c	1.002	0.059	0.524	0.28
By the transformation proposed	1.003	0.041	0.517	0.17

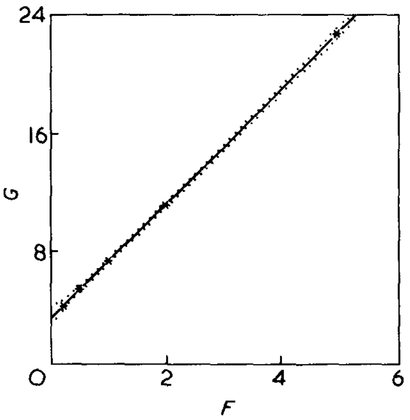

Figure 2 Transformed *G* vs. *F* plot of the measurement presented in *Figure 1* (α = 0.3 g/dl)

from which we have:

$$\gamma = -(x_m + x_M) \tag{10}$$

Calculation with negative values can be avoided by replacing γ by the positive α:

$$\alpha = -\gamma = x_m + x_M \tag{11}$$

Using this expression and after multiplication by -1 the final form of the proposed transformed straight line can be written as

$$G = AF + B \tag{12}$$

where

$$F = -f = \frac{x}{\alpha - x}$$

and

$$G = -g = \frac{y}{\alpha - x} \tag{13}$$

and the parameters are:

$$a = A - B \quad \text{and} \quad b = B\alpha \tag{14}$$

The method proposed is illustrated by an example of viscometric molecular weight determination. A large number of viscometric measurements were carried out on a PVC sample in tetrahydrofuran solution at 25°C, using an Ubbelohde viscosimeter. A Hungarian made industrial suspension PVC sample (Ongrovil S 470) was used (with K = 70, M_n = 54 400, M_w = 97 200, determined by g.p.c.). The results are collected in *Table 1*. The notation in the Table is: $x = c$, the concentration of the solution; $\bar{t}$ is the average of the flow time, each from 30 measurements; F and G are transformed variables calculated according to equation (13) with α = 0.3 g/dl.

In *Figure 1*, the $y = \eta_{sp}/c$ values were plotted, as usual, against concentration. In addition to average values, the standard deviation also calculated from the 30 time measurements has been indicated at each point. The dashed lines were calculated with the standard deviation of all time measurements.

In *Figure 2* the same experimental data are plotted using the proposed transformation. It may be stated that the transformation was effective and the distribution of scatter has been more uniform (identical at the two extreme experimental values). This ensures consideration of the different points with practically identical weight in the determination of parameter values.

The intercept b (the $[\eta]$value of intrinsic viscosity) and the slope a determined from *Figures 1* and *2*, as well as their standard deviations are given in *Table 2*. In *Table 2* it is seen that the intrinsic viscosity and the slope show lower standard deviation with the proposed transformation than in the usual plot. By using the usual plot we have to double the number of measurements to achieve a similar improvement.

CONCLUSIONS

In the determination of the average molecular weight of polymers, extrapolation to zero concentration is customarily carried out with data whose standard deviation increases with a decrease in concentration. The reliability of the determination can be considerably improved by replacing the extrapolation of the usual equation $y = ax + b$ (e.g. π/c vs. c when osmotic pressure or η_{sp}/c vs. c when viscosity is measured) with extrapolation of the linear transformation $G = AF + B$, where $F = x/(\alpha - x)$, $G = y/(\alpha - x)$ and $\alpha = x_m + x_M$ (index m and M denote the lowest and highest values of the independent variable (e.g. concentration), respectively). The suggested transformation results in approximately uniform error distribution and renders extrapolation feasible. Reliability of the parameters is improved to an extent that could be attained only by doubling the number of measurements.

REFERENCES

1 Kelen, T. and Tüdos, F. *Reaction Kinetics Catal. Lett.* 1974, **1**, 487; *J. Macromol. Sci. (A)* 1975, **9**, 1
2 Kennedy J. P., Kelen, T. and Tüdos, F. *J. Polym. Sci. (Polym. Chem. Edn)* 1975, **13**, 2277
3 Tüdos. F., Kelen, T., Földes-Berezsnich, T. and Turcsányi, B. *Reaction Kinetics Catal. Lett.* 1975, **2**, 439; *J. Macromol. Sci. (A)* 1976, **10**, 1507
4 Tudos, F., Kelen, T. and Földes-Berezsnich, T. *J. Polym. Sci. (Polym. Symp.)* 1975, **50** 109
5 Kelen, T., Tüdos, F., Turcsányi, B. and Kennedy, J. P. *J. Polym. Sci. (Polym. Chem. Edn)* 1977, **15**, 3047