

A Polydispersity Corrected Limiting Viscosity Number–Molecular Weight Relationship for Polypropylene Oxide Benzene Solutions

SUMMARY

Using the molecular weight distributions of polydisperse polypropylene oxide fractions determined by gel permeation chromatography a polydispersity corrected limiting viscosity number–molecular weight relationship for polypropylene oxide benzene solutions at 25°C was estimated to be the following $[\eta] = 2.46 \times 10^{-2} M^{0.71}$ ($\text{cm}^3 \text{g}^{-1}$).

Correct estimations of a correlation between two quantities concerning macromolecules is possible only in the case when identical average values of the quantities are taken into account. Especially well known is the influence of the polydispersity of polymers, i.e., of the type and the width of the molecular weight distribution, on average values of the physicochemical quantities.⁷ One of the very popular quantities of polymer systems is the limiting viscosity number $[\eta]$. For chemically homogeneous linear polymers the most important relationship between $[\eta]$ and molecular weight M is the empirical Mark–Houwink–Sakurada equation

$$[\eta] = KM^a \quad (1)$$

where K and a are constants at a given temperature, for a given polymer–solvent system.

Values of M must be obtained by some absolute method in order for K and a to be determined. For polydisperse polymer samples the average values of molecular weights appropriate for eq. (7) are the so-called viscosity-average molecular weights \overline{M}_v ,^{1,2} which are defined as

$$\overline{M}_v = (\sum_i w_i M_i^a)^{1/a} \quad (2)$$

Where w_i are weight fractions of species i in the sample. \overline{M}_v is not an absolute quantity, and, since the parameter a occurs in the defining eq. (2), the viscosity-average molecular weight for a given polymer sample is not only a function of the molecular weight distribution of the sample but also a function of the solvent used.

In view of the fact that monodisperse fractions are very seldom available, in the determination of the K and a parameters, polydispersity of the applied samples should be taken into consideration. The K and a coefficients estimated by different workers for polypropylene oxide benzene solutions at 25°C are scattered.³ It seemed thus worthwhile to determine a more reliable $[\eta]$ – M relationship for this system. In this work experimentally determined molecular weight distributions of a series of polydisperse polypropylene oxide fractions were used for estimation of the polydispersity corrected $[\eta]$ – M relationship.

EXPERIMENTAL

A complete set of experimental data from studies of dilute solution properties of polypropylene oxide made by Valles⁴ was published in a special technical report.⁵ The values of $[\eta]$ and \overline{M}_n of the studied fractions may be found in Table I, where the original designations of Valles were preserved. Fractions numbered 1–6 had been analyzed on one set of GPC columns and the remaining four fractions on another set.

Determination of Molecular Weight Distributions by GPC

Recently, a simple method of accurate GPC calibration was described^{6–8} in which polydisperse samples of practically any polydispersity may be used. Preliminary calibration attempts with chromatograms of the polypropylene oxide fractions of Valles proved that the form of the GPC calibration relations for both sets of columns must be limited to the following linear

TABLE I
Data for Polypropylene Oxide (Taken from Ref. 4)

Fraction no./symbol	$10^{-3} \times \overline{M}_n$	$[\delta]$ (cm ³ /g) benzene (25°C)
1/F-1B1A ^a	922	935
2/F-1B1	588	725
3/F-1B1B	531	575
4/F-1B2	251	360
5/F-2A	232	350
6/F-3A	—	300
7/F-2B	143	203
8/F-2C	54.2	105
9/F-3B	—	75
10/F-4	5.3	21.5

^a $\overline{M}_w = 2.86 \times 10^6$.

equation:

$$V = C_1 - C_2 \log M \quad (3)$$

where V is the retention volume and C_1 and C_2 are constant parameters.

In the above-mentioned calibration method,⁸ the C_1 and C_2 parameters are to be estimated iteratively for a relation between appropriately averaged retention volumes \overline{V} and average molecular weights \overline{M} of the chosen calibration samples. Thus, in the case of polypropylene oxide fractions the corresponding calibration relation was the following:

$$\overline{V}_1 = C_2 - C_2 \log \overline{M}_n \quad (4)$$

where⁸

$$\overline{V}_1 = C_2 \log(\sum_i w_i \times 10^{V_i/C_2}) \quad (5)$$

and w_i are weight fractions of species i corresponding to retention volumes V_i on the chromatogram.

For the first set of columns 1 value of \overline{M}_w and five values of \overline{M}_n together with chromatograms of fractions 1–5 (see Table I) were used for the calibration. The determined calibration relation was the following:

$$V = 49.34 - 4.09 \log M \quad (6)$$

with a standard error of estimate $s = 0.15$ and a coefficient of correlation $r = 0.994$.

Similar calculations were made for fractions 7, 8, and 10, which had been analyzed on the second set of columns. The following calibration relation was obtained:

$$V = 38.06 - 3.01 \log M \quad (7)$$

with $s = 0.02$ and $r = 0.999$.

Using a typical numerical procedure,⁹ the molecular weight distributions and values of \overline{M}_n and of weight average molecular weights, \overline{M}_w , were calculated from the chromatograms of all fractions applying the corresponding calibration eqs. (6) and (7). The obtained values of \overline{M}_n and \overline{M}_w and the percentage deviations of \overline{M}_n computed according to the formula

$$\delta \overline{M}_n (\%) = (\overline{M}_{n,\text{GPC}} - \overline{M}_{n,\text{abs}}) \times 100 / \overline{M}_{n,\text{abs}} \quad (8)$$

may be found in Table II. In eq. (8) $\overline{M}_{n,\text{GPC}}$ and $\overline{M}_{n,\text{abs}}$ denote the \overline{M}_n values calculated from GPC chromatograms or measured by means of an absolute method, correspondingly.

The GPC instrument spreading effects were considered as being negligible because the polypropylene oxide fractions were polydisperse,¹⁰ having values of the $\overline{M}_w/\overline{M}_n$ ratios greater than 3. The above assumption was justified by low values of the calculated $\delta\overline{M}_n$ deviations (compare Table II).

Polydispersity Corrections of the $[\eta]$ - M Relationship

Elias et al.¹ described procedures for estimation of the correct $[\eta]$ - M relationship in case of polydisperse samples in which model analytical molecular weight distributions of the samples were assumed. In this work molecular weight distributions of the polypropylene oxide fractions were determined experimentally therefore no assumptions were needed.

The polydispersity correction procedure was basically the same as described by Elias et al.¹ The starting step was a least squares determination of initial values of the K and a parameters for the relationship $[\eta]-\overline{M}_n$, in which, for a chosen set of polypropylene oxide fractions with numbers 1,3,5,7,8, and 10 (compare Table I), the following results were obtained:

$$[\eta] = 3.89 \times 10^{-2} \overline{M}_n^{0.73} \text{ (cm}^3/\text{g)} \quad (9)$$

Next, an iteration procedure was started where in each iteration step the temporary values of \overline{M}_v of the samples used in the calculations were evaluated according to eq. (2), taking advantage of the known molecular weight distributions and of the last value of a . Then a new least squares determination of the parameters K and a was made. After five iterations the parameters were estimated with a relative accuracy better than 10^{-5} and the following polydispersity corrected $[\eta]-\overline{M}$ relationship for the polypropylene oxide solutions in benzene at 25°C was obtained

$$[\eta] = 2.49 \times 10^{-2} \overline{M}_v^{0.71} \text{ (cm}^3/\text{g)} \quad (10)$$

Using the molecular weight distributions of all polypropylene oxide fractions and taking advantage of the K and a parameters from eq. (10) values of $[\eta]$ were calculated according to a formula:

$$[\eta] = K \sum_i w_i M_i^a \quad (11)$$

where values of M_i were computed for given V_i according to the corresponding GPC calibration equation (6) or (7). The obtained results together with percentage deviations of $[\eta]$ calculated

TABLE II
Results of GPC Analysis of Polypropylene Oxide Polydisperse Fractions (Chromatograms Taken from Ref.⁵)

Fraction no.	$10^{-3} \times \overline{M}_n$	$\delta \overline{M}_n$ (%)	$[\eta]$ (cm ³ /g) eq. (10)	$\delta [\eta]$ (%)
1	905	-1.8	874	-6.5
3	479	-9.8	579	0.7
5	246	6.0	366	4.6
7	141	-1.4	215	5.9
8	54.5	0.6	106	1.0
10	5.25	-1.0	20.8	-3.3
2	539	-8.3	730	0.7
4	263	4.8	401	11.4
6	176	—	348	16.0
9	15.6	—	84.6	12.8

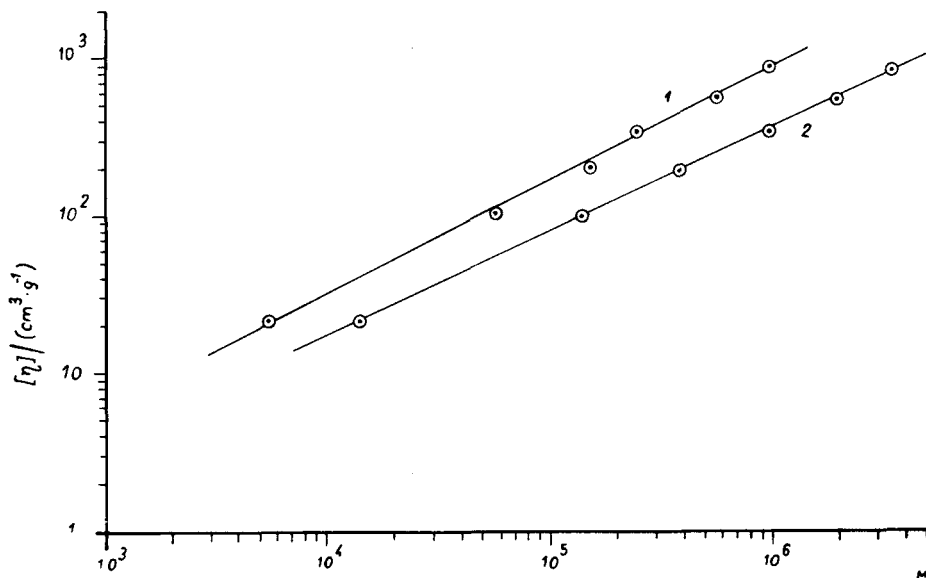


Fig. 1. Limiting viscosity number-molecular weight relationships for polypropylene oxide solutions in benzene at 25°C: (1) $c[\eta]$ and \overline{M}_n ; (2) $[\eta]$ and \overline{M}_v .

from a formula analogous to eq. (8) may be found in Table II. The initial $[\eta]-\overline{M}_n$ and the final $[\eta]-\overline{M}_v$ relationships are presented graphically in Figure 1.

Results obtained in this work may be considered as satisfactory. The percentage deviations of \overline{M}_n and of $[\eta]$ are relatively small Table II. The good results prove that a correct limiting viscosity number-molecular weight relationship may be determined for polydisperse samples with different polydispersities when molecular weight distributions of the samples are determined

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