

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Determination of the Sedimentation Coefficient-Molecular Weight Relation for Nonideal Systems Based on Sedimentation and Viscosity Measurements of a Few Unfractionated Samples

Pawel Szewczyk^{ab}; Maurycy Kalfus^a

^a Research and Development Department, Chemical Works, Oświęcim, Poland ^b Polish Academy of Sciences, Research Center, Institute of Polymer Chemistry, Zabrze, Poland

To cite this Article Szewczyk, Pawel and Kalfus, Maurycy(1973) 'Determination of the Sedimentation Coefficient-Molecular Weight Relation for Nonideal Systems Based on Sedimentation and Viscosity Measurements of a Few Unfractionated Samples', Journal of Macromolecular Science, Part A, 7: 3, 737 – 752

To link to this Article: DOI: 10.1080/00222337308061167

URL: <http://dx.doi.org/10.1080/00222337308061167>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Determination of the Sedimentation Coefficient-Molecular Weight Relation for Nonideal Systems Based on Sedimentation and Viscosity Measurements of a Few Unfractionated Samples

PAWEŁ SZEWCZYK* and MAURYCY KALFUS

Research and Development Department
Chemical Works
Oświęcim, Poland

ABSTRACT

A new method for the determination of the sedimentation coefficient-molecular weight relation is proposed. Based on the very low sensitivity of the corresponding sedimentation coefficient average $\bar{S}_{0,1}$ and the weight-average molecular weight \bar{M}_w (calculated according to the generalized Flory-Mandelkern equation) to changes of the a_s parameter, the $\bar{S}_{0,1}$ and \bar{M}_w values are estimated from constant initial values of the a_s parameter for all those polymer-solvent systems for which the real a_s values do not exceed the interval 0.3-0.5. The approximations involved give an error lower than 8.5%, i.e., below the experimental errors of

*Present address: Polish Academy of Sciences, Research Center, Institute of Polymer Chemistry, P.B. 49, ul. Hagera 17, Zabrze, Poland.

the M_w values determined for polydisperse samples. The new method of determining the S_0 - M relation was applied to the system styrene-acrylonitrile copolymer (22.6-wt% acrylonitrile content) in acetone at 25°C and yielded the following relation: $S_0 = 2.90 \times 10^{-13} M^{0.49}$ sec. Although in the case of this polymer-solvent system the a_s value of 0.49 is close to the one corresponding to θ systems, the method is shown by model calculations to be of general applicability and especially useful in the case of nonideal polymer-solvent systems.

In previous works [1, 2] two new methods for establishing the sedimentation coefficient-molecular weight relation in nonideal polymer-solvent systems

$$S_0 = K_s M^{a_s} \quad (1)$$

from sedimentation data of unfractionated samples have been presented. In Eq. (1) S_0 , M , K_s , and a_s are the sedimentation coefficient at infinite dilution, the molecular weight, and empirical constants, respectively. The method based on sedimentation data for a single unfractionated sample proved unsuccessful owing to concentration effects. The second method, based on sedimentation data for pairs of unfractionated samples, yielded promising data. An attempt to apply the second method to a commercial copolymer of styrene and acrylonitrile in acetone resulted in the development of the new method presented here.

THEORETICAL

In order to find the K_s and a_s constants in the case of unfractionated samples, a certain average value of sedimentation coefficient $\bar{S}_{0,1}$ and/or $\bar{S}_{0,2}$ should be computed from the following relations [3, 4] by using a preliminary estimate of a_s :

$$\bar{S}_{0,1} = \left[\sum_i w_i S_{0,i}^{1/a_s} \right]^{a_s} \quad (2)$$

and

$$\bar{S}_{0,2} = \left[\sum_i w_i S_{0,i}^{-1/a_s} \right]^{-a_s} \tag{3}$$

where $S_{0,i}$ and w_i represent the sedimentation coefficient at infinite dilution and atmospheric pressure and the weight fraction of component i of the heterogenous polymer.

From the plot of $\log \bar{M}_w$ vs $\log \bar{S}_{0,1}$ and/or $\log \bar{M}_n$ vs $\log \bar{S}_{0,2}$, a_s and K_s can be found. \bar{M}_w and \bar{M}_n are weight- and number-average molecular weights, respectively. If necessary, the values of $\bar{S}_{0,1}$ and/or $\bar{S}_{0,2}$ can be recomputed after a_s has been determined. The necessity of processing data for a number of samples with \bar{M}_w and/or \bar{M}_n values covering a broad range of molecular weights is the basic disadvantage of the above method.

Based on the π -theorem [5], the following relations are easily obtained:

$$\bar{M}_{w,1} / \bar{M}_{w,2} = \left[\sum_i w_{i,1} S_{0i,1}^{1/a_s} \right] / \left[\sum_j w_{j,2} S_{0j,2}^{1/a_s} \right] \tag{4}$$

$$\bar{M}_{n,1} / \bar{M}_{n,2} = \left[\sum_j w_{j,2} S_{0j,2}^{-1/a_s} \right] / \left[\sum_i w_{i,1} S_{0i,1}^{-1/a_s} \right] \tag{5}$$

where the indexes 1 and 2 mark two samples with different values of \bar{M}_w or \bar{M}_n . Furthermore, it is possible to calculate both \bar{M}_w and \bar{M}_n for polydisperse samples from measurements of the sedimentation coefficients $S_{0,i}$, their weight fractions w_i , and the limiting viscosity numbers $[\eta]$ [6], since

$$\bar{M}_w = K_{s\eta} ([\eta])^{0.5} \left(\sum_i w_i S_{0i}^{1/a_s} \right) \left(\sum_i w_i S_{0i}^{(2-3a_s)/a_s} \right)^{-0.5} \tag{6}$$

and

$$\bar{M}_n = K_{s\eta} ([\eta])^{0.5} \left(\sum_i w_i S_{0i}^{-1/a_s} \right)^{-1} \left(\sum_i w_i S_{0i}^{(2-3a_s)/a_s} \right)^{-0.5} \tag{7}$$

where

$$K_{S\eta} = \left[N_a \eta_0 / \phi^{1/3} P^{-1} (1 - \bar{v} \delta_0) \right]^{1.5} \quad (8)$$

In Eq. (8) \bar{v} is the partial specific volume of the polymer in a given solvent, δ_0 is its density, and η_0 is its viscosity; N_a and $\phi^{1/3} P^{-1}$ are the Avogadro and Mandelkern-Flory constants, respectively.

Combining Eqs. (4) and (6) as well as Eqs. (5) and (6) gives

$$[\eta]_1 / [\eta]_2 = \left(\sum_i w_{i,1} S_{oi,1}^{(2-3a_s)/a_s} \right) / \left(\sum_j w_{j,2} S_{oj,2}^{(2-3a_s)/a_s} \right) \quad (9)$$

Equation (9) contains a_s as the only unknown value, and it can be found by an iteration procedure since $a_s \leq 0.5$. Given a_s , one can compute \bar{M}_w and/or \bar{M}_n as well as $\bar{S}_{o,1}$ and/or $\bar{S}_{o,2}$ and finally K_s as

$$\bar{S}_{o,i} = K_s \bar{M}_k^{a_s} \quad (10)$$

Here $k = w$ for $i = 1$ and $k = n$ for $i = 2$.

EXPERIMENTAL

Materials and Procedures

As the test material the Dows styrene-acrylonitrile (SAN) copolymer Tyrl 760 (22.8-wt% acrylonitrile content) was used. Reagent-grade solvents were employed. Without using additional treatment, SAN samples with different average molecular weights but of practically the same average chemical composition were used in broad fractions obtained by a coarse preparative fractionation with chloroform-ethanol as a solvent-nonsolvent system. The method of Shimura et al. [7, 8] was applied. Agreement of the chemical composition of each fraction with the average one was confirmed by the determination of nitrogen content by Kjeldahl's method.

Viscosity measurements were carried out in an Ubbelohde-type dilution viscometer for the SAN copolymer and its fractions in acetone at $25 \pm 0.02^\circ\text{C}$. The data were processed either according to

the generally used Huggins [9] and Kraemer [10] equations or according to a method proposed by Maron and Reznik [11]. The value of 0.204 for the buoyancy factor $(1 - \bar{v} \delta_0)$ in acetone at $25 \pm 0.2^\circ\text{C}$ was obtained from pycnometric measurements. Sedimentation of the original sample and of its seven fractions in acetone at $25 \pm 0.1^\circ\text{C}$ was done in a Spinco model E analytical ultracentrifuge. All measurements were carried out with a 30-mm single-sector cell at a relatively low angular velocity of 29,500 rpm, which meant the pressure effects on the sedimentation coefficients could be disregarded. The sedimentation boundary coordinates on schlieren photographs were measured with a two-dimensional microcomparator [12]. The distributions of sedimentation coefficients at infinite dilution and at infinite time were obtained by the method of sedimentation analysis described by Homma et al. [13, 14]. Estimation of the zero-time correction for the initial SAN copolymer and for all its fractions was necessary. The estimation was made using the procedure of Elias [15]. Probably due to electrostatic induction forces acting between neighboring groups of the copolymer chain, the actual sedimentation of the macromolecules in acetone started only after the full rotor speed was attained.

Results

The weight fractions, the acrylonitrile content, the limiting viscosity number $[\eta]$, and the Huggins constant k' (measured in acetone at 25°C) of the initial, i.e., unfractionated, copolymer (No. 0) and its seven fractions are given in Table 1.

The fractionation data were checked by computing the intrinsic viscosity $[\eta]$ of the parent polymer from

$$[\eta] = \sum_{i=1}^{i=7} w_i [\eta]_i$$

where $[\eta]_i$ and w_i are the limiting viscosity numbers (Table 1, Column 5) and weight fractions (Table 1, Column 3) of the fractions, respectively. The obtained $[\eta]$ (0.483) was very close to the limiting viscosity number (0.503) of the parent polymer.

The fractions 1, 2, 5, and 6, having approximately the same average acrylonitrile content, were used for further analysis. Plots of the sedimentation coefficient distributions at infinite time and at infinite dilution for these fractions are shown in Fig. 1.

With known values of $[\eta]$, w , and S_0 for pairs of SAN fractions, the a_s parameter was calculated according to Eq. (9) using an iteration procedure. A corresponding Algol-60 program was written for the Polish

TABLE 1. Preliminary Results for SAN-Tyrl 760

Fraction No.	Fraction weight (g)	Weight fraction (%)	AN content (wt%)	$[\eta]$ ($100 \text{ cm}^3 \text{ g}^{-1}$)	k'
0 ^a	6.000	100	22.8	0.508	0.43
1	0.853	15.4	22.4	0.763	0.44
2	0.641	11.6	22.7	0.650	0.53
3	0.539	9.7	27.7	0.595	0.58
4	0.462	8.3	25.0	0.549	0.47
5	0.783	14.1	22.7	0.514	0.30
6	1.046	18.9	22.4	0.365	0.11
7	1.223	22.0	24.4	0.206	0.15
Loss	0.453	0	-	-	-

^aUnfractionated sample.

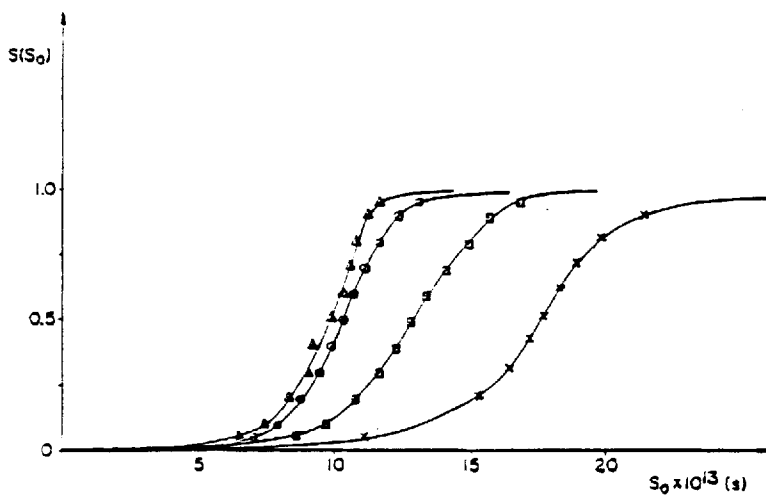


FIG. 1. Integral distributions $G(S_0)$ of sedimentation coefficients S_0 for SAN copolymer in acetone at 25°C : (\times) Fraction 1, (\square) Fraction 2, (\circ) Fraction 5, and (\triangle) Fraction 6.

ZAM-41 computer. Calculations started with $a_s = 0.5$ and continued until the value of a_s was established with an accuracy of ± 0.001 . When the a_s value was found, the $\bar{S}_{0,1}$ average sedimentation coefficient and the weight-average molecular weight \bar{M}_w were calculated using Eqs. (2) and (6), respectively. The value of the constant parameter $K_{S\eta}$ (Eq. 8) for SAN copolymer in acetone at 25°C was 6970, sedimentation coefficients being expressed in 10^{-13} sec and limiting viscosity numbers in $100\text{ cm}^3\text{ g}^{-1}$. The factor $\phi^{1/3}P^{-1}$ is a constant supposed to be independent of the particular polymer-solvent system employed. Numerous experimental evaluations [16-19] indicate the approximate constancy of $\phi^{1/3}P^{-1}$ is an average value of 2.5×10^6 for polymers having a random coil configuration. Although the value of $\phi^{1/3}P^{-1}$ may differ with molecular configuration and may not be entirely constant within a particular polymer-solvent system [20, 21], Eq. (6) can be useful, however, for calculations of approximate molecular weights. In the present work the average value of 2.5×10^6 for the factor $\phi^{1/3}P^{-1}$ in Eq. (8) was used.

Values of the a_s parameter, the $\bar{S}_{0,1}$ average sedimentation coefficient, and the weight-average molecular weight \bar{M}_w are given in Table 2.

TABLE 2. Iteration Results for a_s Parameter and Values of $\bar{S}_{0,1}$ and \bar{M}_w for Given a_s Values

Pair of fractions	$[\eta]_1/[\eta]_2$	a_s	No. of fraction	$\bar{S}_{0,1} \times 10^{13}$ (sec)	$\bar{M}_w \times 10^{-5}$
1, 2	1.18	0.565	1	18.12	4.737
			2	13.41	2.781
1, 5	1.49	0.534	1	18.16	4.763
			5	10.59	1.736
1, 6	2.09	0.478	1	18.25	4.808
			6	9.23	1.289
2, 5	1.26	0.501	2	13.47	2.810
			5	10.61	1.745
2, 6	1.78	0.419	2	13.58	2.844
			6	9.77	1.296
5, 6	1.41	0.304	5	10.87	1.773
			6	9.89	1.301

Results for a_s obtained from experimental data for pairs of samples which differ in $[\eta]$ values from one another are unsatisfactory. However, the very low sensitivity of $\bar{S}_{0,1}$ and \bar{M}_w values to changes of the a_s parameter are quite striking (see Table 2, Columns 3, 5, and 6). It was this fact that was the subject of further study and the chief feature of our new method.

Dependence of $\bar{S}_{0,1}$ and \bar{M}_w on the a_s Parameter

Three theoretical models of sedimentation coefficient distributions were used to examine the sensitivity of $\bar{S}_{0,1}$ and \bar{M}_w to changes of the a_s parameter in a general way. The models were: a pauci-disperse distribution composed of two or three monodisperse fractions, the Gaussian model, and the Schulz-Zimm model, supposed to be the best mathematical approximation of real sedimentation coefficient distributions [22]. The values of $\bar{S}_{0,1}$ and $R = K_{s\eta}^{-1}([\eta])^{-0.5} \bar{M}_w$ were tabulated for the above distributions, as were a_s values from 0.2 to 0.6 with intervals of 0.02. A narrower interval of a_s values than, say, 0.3-0.5 was chosen because of the good resolving power of the ultracentrifuge and for theoretical requirements. In the case of the Gaussian and Schulz-Zimm models, the intervals of sedimentation coefficient values were chosen about a typical synthetic polymers value of 10×10^{-13} sec so that the area under the above-mentioned normalized model distributions exceeded 0.99. Parameters of the nine variants of the Schulz-Zimm model used were chosen so that the values of the \bar{M}_w/\bar{M}_n ratios, calculated for those variants, covered the interval 1.5-50, i.e., the entire interval usually encountered with synthetic polymers [23]. Figures 2 and 3 show plots of $\bar{S}_{0,1}$ vs a_s and of R vs a_s , respectively, for five chosen variants of the Schulz-Zimm model.

As can be seen in Fig. 2, the $\bar{S}_{0,1}$ average sedimentation coefficient in the interval of a_s values considered is a monotonically decreasing function of a_s . The weight-average molecular weight \bar{M}_w has a maximum value at $a_s = 1/3$ for any kind of sedimentation coefficient distribution [24].

In order to make a rough quantitative analysis of the $\bar{S}_{0,1}$ - a_s and \bar{M}_w - a_s dependencies, the values of arithmetic averages of $\bar{S}_{0,1}$ and R were calculated. In the case of $\bar{S}_{0,1}$ the arithmetic average was calculated for

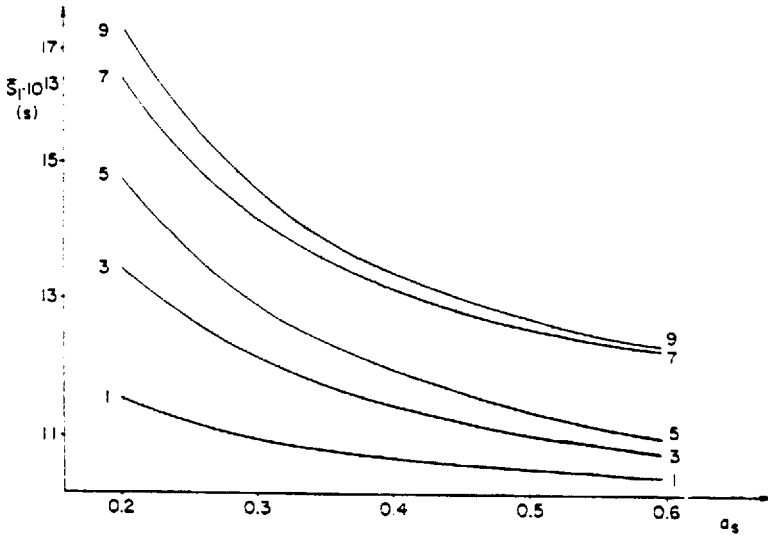


FIG. 2. Plots of the $\bar{S}_{0,1}$ - a_s dependence for the Schulz-Zimm model of sedimentation coefficient distributions: $\bar{M}_w/\bar{M}_n = 1.47$ (1), 2.97 (3), 6.00 (5), 13.6 (7), and 53.2 (9).

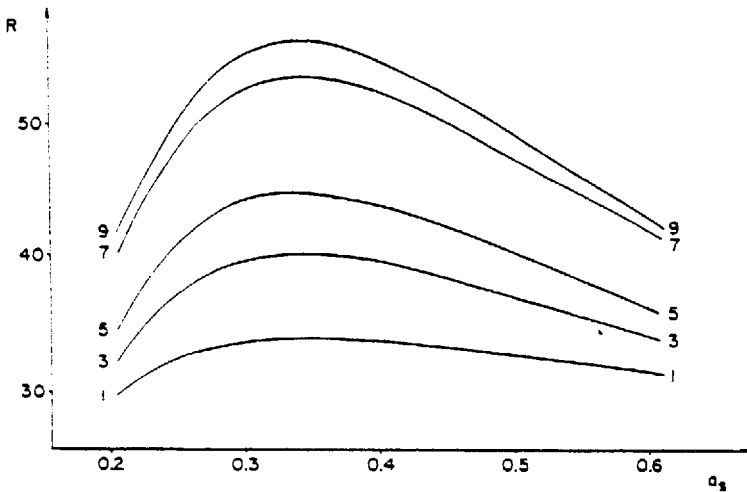


FIG. 3. Plots of the \bar{M}_w - a_s dependence for the same variants of the Schulz-Zimm model as in Fig. 2. (Note: $R = \bar{M}_w K_{s\eta}^{-1} [\eta]^{-0.5}$.)

Downloaded At: 10:21 25 January 2011

values of $\bar{S}_{0,1}$ at $a_s = 0.3$ and 0.5 , and in the case of R for values of R at $a_s = 0.34$ (maximum value) and 0.5 , respectively. The maximum relative deviations from the above-mentioned average values in the corresponding a_s intervals were then calculated both for $\bar{S}_{0,1}$ and R . The results obtained for the maximum sedimentation coefficient δS_0 and molecular weight δM deviations of nine variants of the Schulz-Zimm model distribution are given in Table 3.

TABLE 3. Maximum Deviations of the Sedimentation Coefficients $\bar{S}_{0,1}$ and Molecular Weights \bar{M}_w from Their Corresponding Average Values in the a_s Interval 0.3-0.5 for the Schulz-Zimm Model Sedimentation Coefficient Distributions

Variant No.	\bar{M}_w/\bar{M}_n	δS_0 (%)	δM (%)
1	1.47	2.7	2.0
2	2.10	4.5	3.3
3	2.97	6.0	4.3
4	4.20	6.1	5.0
5	6.00	7.9	5.5
6	8.30	6.7	6.0
7	13.6	7.3	6.4
8	23.4	7.8	6.7
9	53.2	8.3	6.9

An analysis identical to the one described above was made for experimental sedimentation coefficient distributions for the SAN copolymer. The results for the δS_0 and δM deviations of the four SAN fractions investigated are given in Table 4.

In the a_s interval of 0.3-0.5 the average value of the $\bar{S}_{0,1}$ sedimentation coefficients for all model distributions as well as for the experimental ones was approximately equal to the value of $\bar{S}_{0,1}$ for $a_s = 0.38$. In the case of the \bar{M}_w molecular weights the average R

TABLE 4. Maximum δS_0 and δM Deviations in the a_s Interval 0.3-0.5 for SAN Copolymer Fractions

Fraction No.	δS_0 (%)	δM (%)
1	1.3	1.0
2	1.4	1.0
5	0.8	0.8
6	0.9	0.6

values in the a_s interval of 0.34-0.5 were approximately equal to R at $a_s = 0.44$ for all distributions considered.

DISCUSSION AND CONCLUSIONS

The practically inevitable errors in the determination of average sedimentation coefficients or average molecular weights amount to 10% or more in the case of polydisperse samples [23]. Analysis of the dependence on the a_s parameter of the $\bar{S}_{0,1}$ average sedimentation coefficient and the weight-average molecular weight calculated according to Eq. (6) has shown that, for various theoretical and experimental sedimentation coefficient distributions, the calculation of the $\bar{S}_{0,1}$ average with $a_s = 0.38$ and \bar{M}_w with $a_s = 0.44$ results in an error not exceeding 8.5% in the a_s interval of practical importance, 0.3-0.5. The errors are thus smaller than errors of the experimental determination of average molecular weights. On the basis of these facts a new method for the S_0 -M relation determination for any polymer-solvent system was proposed. This method should prove especially useful in cases of polymers for which it is very difficult or virtually impossible to find pseudoideal conditions. The novelty of the proposed method lies in the fact that in calculations of the corresponding average sedimentation coefficients ($\bar{S}_{0,1}$) and average molecular weights (\bar{M}_w) the constant initial values of the a_s parameter, i.e., 0.38 and 0.44, respectively, may be used for every polymer-solvent system. The average molecular weights are calculated according to the Flory-Mandelkern equation.

Once the values of $\bar{S}_{0,1}$ and \bar{M}_w for a few polydisperse polymer

samples are established, the least-squares S_0 - M relation may be calculated. And thus, using the generalized Flory-Mandelkern Eqs. (6) or (7) for the evaluation of average molecular weights and the constant initial estimates of the a_s values, the time-consuming experimental measurements of \overline{M}_w or \overline{M}_n may be avoided. Evaluation of average molecular weights based on sedimentation coefficient distributions diminishes the effects of the experimental cut-off errors [22, 25], because identical cut-offs influence the average sedimentation coefficients and the average molecular weights. The S_0 - M relation is determined for pairs of the S_0 and M averages.

The proposed method was used in the S_0 - M relation determination for the SAN copolymer in acetone at 25°C. The sedimentation and viscosity data for the four analyzed fractions (compare Fig. 1) were thus used to calculate the $\overline{S}_{0,1}$ and \overline{M}_w averages with the appropriate a_s parameter values. Finally, the following least squares S_0 - M relation was estimated

$$S_0 = 2.90 \times 10^{-13} M^{0.49} \text{ sec} \quad (11)$$

The $\overline{S}_{0,1}$ average values used in the determination of Eq. (11) covered the interval $(9.8-18.5) \times 10^{-13}$ sec and the \overline{M}_w values that of $(1.3-4.8) \times 10^5$. The use of constant initial a_s values instead of the correct one, i.e., $a_s = 0.49$, in the evaluation of the $\overline{S}_{0,1}$ and \overline{M}_w averages introduced errors not exceeding 1.4% for the SAN copolymer-acetone system.

The distributions of sedimentation coefficients of the SAN fractions (Fig. 1) were transformed into the molecular weight distributions by Eq. (11). The resulting molecular weight distribution curves are shown in Fig. 4.

The weight- and number-average molecular weights as well as their ratios were calculated from the molecular weight distributions of the four SAN copolymer fractions. The values obtained for \overline{M}_w , \overline{M}_n , and $\overline{M}_w/\overline{M}_n$ are listed in Table 5, together with the $\overline{S}_{0,1}$ and \overline{M}_w average values (the last one calculated according to Eq. 6) for $a_s = 0.49$.

As can be seen in Table 5, weight-average molecular weights obtained by the use of Eq. (6) with the appropriate value of the a_s parameter agree very well with those obtained from the molecular weight distributions. This agreement may be considered to support the value of 2.5×10^9 assumed for the $\phi^{1/3} P^{-1}$ constant, and thus

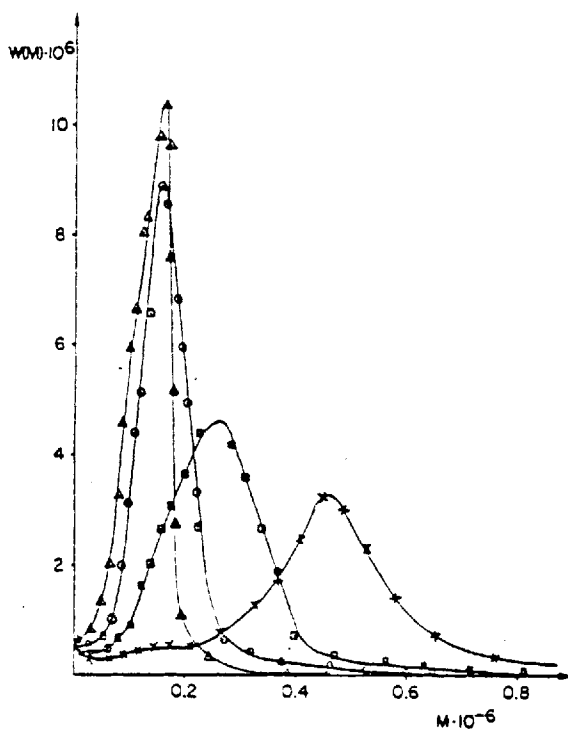


FIG. 4. Differential molecular weight distribution curves of SAN copolymer fractions. Data are identified as in Fig. 1.

provide another example of the practical applicability of Eq. (6) in the evaluation of weight-average molecular weights and, finally, the S_0 - M relation for any polymer-solvent system.

In order to make additional comparison of average molecular weights obtained by different methods, the relation given by Elias and Bareiss [27] valid for the theta state

$$\bar{M}_v = K_{s\eta} \left(\sum_i w_i S_{oi} \right)^{1.5} [\eta_i]^{0.5} \quad (12)$$

was applied for the SAN copolymer-acetone system at the close-to- θ temperature of 25°C. In Eq. (12) all parameters have the same meaning as in Eq. (6), and \bar{M}_v denotes the viscosity-average molecular

TABLE 5. Sedimentation Coefficients and Molecular Weights for SAN-Tyrl 760 Fractions

Fraction No.	$\bar{S}_{0,1} \times 10^{13}$ (sec)	\bar{M}_w	\bar{M}_w (Eq. 6)	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	13.30	502,500	480,100	145,700	3.49
2	13.53	271,200	281,400	146,900	1.85
5	10.66	165,100	174,700	110,900	1.49
6	9.74	123,800	128,700	70,900	1.79

weight. On the other hand the \bar{M}_v average was calculated from the molecular weight distribution (MWD) data from the relation

$$\bar{M}_v = \left(\sum_i w_i M_i^{a_\eta} \right)^{1/a_\eta} \quad (13)$$

with $a_\eta = 0.5$ being the power index in the Mark-Houwink relation at the theta conditions.

Results obtained for the four SAN-Tyrl 760 fractions are given in Table 6 together with values of \bar{M}_w and \bar{M}_n obtained from the MWD data as well as \bar{M}_w calculated according to Eq. (6).

Values of the viscosity-average molecular weights \bar{M}_v obtained from MWD data (Table 6, Column 4) compare well with those calculated

TABLE 6. Average Molecular Weights for SAN-Tyrl 760 Copolymer Fractions

Fraction No.	\bar{M}_w (MWD)	\bar{M}_w (Eq. 6)	\bar{M}_v (Eq. 13)	\bar{M}_v (Eq. 12)	\bar{M}_n (MWD)
1	502,500	480,100	475,100	457,200	145,700
2	271,200	281,400	258,900	274,100	146,900
5	165,100	174,700	159,100	167,600	110,900
6	123,800	128,700	111,500	108,600	70,900

according to the modified Flory-Mandelkern Eq. (12) (Table 6, Column 5). The actual differences between these two \bar{M}_v values do not exceed 6%, which proves the applicability of the proposed method of establishing the S_0 -M relation in the case of new polymer-solvent systems.

The practical application of sedimentation velocity analysis for the determination of a molecular weight distribution appears to depend to a certain extent upon the solvent employed. It was found that at the concentrations required for most sedimentation measurements, a better molecular separation could be obtained by the use of a θ or a close-to- θ solvent [26]. Acetone as a solvent of the SAN copolymer is not a good solvent (the a_s value of 0.49 is close to 0.5, corresponding to θ solvents), which assures a high resolving power in the sedimentation velocity experiments.

Finally, it should be noted that the constant initial values of the a_s parameter may be used to calculate the corresponding average sedimentation coefficients and average molecular weights of a pair of samples. However, the above-mentioned experimental inaccuracy and the data processing errors give unreliable estimates of the a_s and K_s values when based on data for a single pair of samples only. The observed large differences of the a_s values estimated for pairs of samples of the same polymer (see Table 2, Column 3) are due to the very low sensitivity of $\bar{S}_{0,1}$ and \bar{M}_w averages to changes of the a_s parameter, and therefore even small errors made in the estimation of \bar{M}_w and $[\eta]$ result in a significant scatter of the a_s values.

REFERENCES

- [1] M. Kalfus and P. Szewczyk, Rocz. Chem., **42**, 1367 (1968).
- [2] P. Szewczyk and M. Kalfus, Rocz. Chem., **43**, 1711 (1969).
- [3] R. L. Baldwin and K. E. van Holde, Fortschr. Hochpolym. Forsch., **1**, 451 (1960).
- [4] H. W. McCormick, J. Polym. Sci., Part A, **1**, 103 (1963).
- [5] H.-G. Elias and M. Kalfus, Makromol. Chem., **105**, 95 (1967).
- [6] M. Kalfus and H.-G. Elias, J. Macromol. Sci.—Chem., **A1**, 955 (1967).
- [7] Y. Shimura, I. Mita, and H. Kambe, J. Polym. Sci., **2**, 403 (1964).
- [8] Y. Shimura, J. Polym. Sci., Part A-2, **4**, 423 (1966).
- [9] M. L. Huggins, J. Amer. Chem. Soc., **64**, 2716 (1942).
- [10] E. O. Kraemer, Ind. Eng. Chem., **30**, 1200 (1938).
- [11] S. H. Maron and R. B. Reznik, J. Polym. Sci., Part A-2, **7**, 309 (1969).

- [12] M. Kalfus, Prib. Tekh. Eksp., **2**, 185 (1965).
- [13] T. Homma, K. Kawahara, H. Fujita, and M. Ueda, Makromol. Chem., **67**, 132 (1963).
- [14] T. Homma and H. Fujita, J. Appl. Polym. Sci., **9**, 1071 (1965).
- [15] H.-G. Elias, Makromol. Chem., **30**, 48 (1959).
- [16] L. Mandelkern and P. J. Flory, J. Chem. Phys., **20**, 212 (1952).
- [17] L. Mandelkern, W. R. Krigbaum, H. A. Scheraga, and P. J. Flory, J. Chem. Phys., **20**, 1392 (1952).
- [18] T. G. Fox and L. Mandelkern, J. Chem. Phys., **21**, 187 (1953).
- [19] H. A. Scheraga and L. Mandelkern, J. Amer. Chem. Soc., **75**, 179 (1953).
- [20] M. Kurata and H. Yamakawa, J. Chem. Phys., **29**, 311 (1958).
- [21] W. H. Stockmayer and A. C. Albrecht, J. Polym. Sci., **32**, 215 (1958).
- [22] A. M. Kotliar, J. Polym. Sci., Part A, **2**, 4303 (1964); Ibid., Part A, **2**, 4327 (1964).
- [23] F. W. Billmeyer, Jr., J. Polym. Sci., Part C, **8**, 161 (1965).
- [24] P. Szewczyk, Ph.D. Thesis, Chemical Works, Oświęcim, 1971.
- [25] M. Kalfus and J. Mitus, J. Polym. Sci., Part A, **4**, 953 (1966).
- [26] H. W. McCormick, in Polymer Fractionation (M. J. R. Cantow, ed.), Academic, New York, 1967, p. 251.
- [27] H.-G. Elias and R. Bareiss, J. Macromol. Sci.-Chem., **A1**, 1377 (1967).

Received for publication October 10, 1972