Characterization of Polystyrenes of Extremely High Molecular Weights[†]

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ABSTRACT: An extensive effort to characterize polystyrenes of a wide range of molecular weights of up to $M_w = 40 \times 10^6$ by a variety of different methods is reported. The employed methods of investigation, such as frequency analyzing (dynamic) and frequency averaging (classical) light scattering, velocity sedimentation, and viscometry, always lead to linear double-logarithmic relationships between the obtained quantities and the molecular weight. Molecular weight distributions of several samples in the same molecular weight range were investigated as well by classical light scattering, velocity sedimentation, and GPC. Comparison of the results, also with fractionation data, gives good agreement between the different methods and demonstrates the usefulness of some new approaches.

Until recently, synthetic polymers of extremely high molecular weights have only been of limited interest to the scientific world, even though an extension of the molecular weight scale by one or two decades might provide a crucial experimental test for some theoretical equations, e.g., relating the conformation to the excluded volume.

There are, however, a number of problems associated with the investigation of the properties of extremely high molecular weight polymers: For one, the systematic preparation of such polymers requires in general a rather refined experimental technique which must meet the most stringent purity specifications, irrespective of the mode of synthesis. Anionic polymerization has been advanced systematically to yield polystyrenes in the molecular weight range of $M_w = 13 \times 10^6$ with narrow molecular weight distributions (MWD).[1] Earlier, McIntyre et al.[2] had been successful in obtaining an anionic polystyrene of $M_w = 44 \times 10^6$. Emulsion polymerization just recently yielded a polystyrene of $M_w = 57 \times 10^6$ after fractionation.[3] Purely thermal polymerization of styrene at low temperatures to low conversion leads to polymers of similarly high molecular weights ($M_w = 35 \times 10^6$ unfractionated).[4] Spontaneous thermal polymerization of methyl methacrylate at lower temperatures produces polymers in the same or possibly higher molecular weight range.[5] The latter two modes of polymerization yield molecular weight distributions of $M_w/M_n = 2$, since their molecular weights are regulated by transfer reactions to an intermediate and/or the monomer, respectively.

Isolation of the polymer from the reaction mixture[2] and subsequent handling such as freeze-drying[6] demand caution in order to avoid degradation which in turn could lead to erroneous results. Fractionation of such polymers is extremely tedious[3] and, depending on the employed solvent system, may be accompanied by excessive degradation.[4]

Yet, most difficulties probably arise during the actual characterization since most techniques for the determination of molecular weights and their distributions have previously been restricted to molecular weights of up to approximately 5×10^6 or less. Several methods of investigation may serve as potential tools for the desired molecular weight determinations: frequency averaging (FAV) and frequency analyzing (FAN) light scattering, ultracentrifugation methods, electron microscopy,[7] viscometry, and gel permeation chromatography (GPC). All of the above methods, except for the viscometry, can also be readily employed to determine the molecular weight distribution, though not necessarily with the same apparatus.

Commercial light scattering photometers to determine the molecular weight (FAV or classical light scattering) are usually not designed to measure down to low scattering angles, θ, or, alternatively, to measure at higher wavelength, λ, a prerequisite for this problem. Therefore, specifically designed photometers to meet those demands have been built in the respective laboratories.[2,3,8] Equilibrium sedimentation also yields M_w, but extremely large run times, even at low column heights, are encountered.[2]

Viscometry becomes increasingly cumbersome as molecular weights increase, demanding more elaborate gradient measurements,[9] but the Mark–Houwink relationship has been shown to remain linear to at least $M_w = 40 \times 10^6$.[10] GPC has been successfully employed to characterize narrow polystyrenes of molecular weights up to 13×10^6,[1] whereas Slagowski et al.[11] found that their sample of $M_w = 44 \times 10^6$ degraded in their GPC.

It will be shown that most methods can be adapted to the characterization of polystyrenes of up to $M_w = 40 \times 10^6$. In addition, FAN light scattering (diffusion coefficient), FAV light scattering, and Svedberg's equation have been employed to describe the MWD of the available samples.

Experimental Section

Materials. Anionic polystyrenes were purchased from two sources: Pressure Chemical Co., Pittsburgh, Pa. (abbreviated as PCC), and Toyo Soda Manufacturing Co., Tokyo (TSK). Molecular weights are given as multiples of a million in a suffix, e.g., TSK $M_w = 7\,500\,000$ will be given as TSK 7.50.

Thermally polymerized polystyrenes were prepared and fractionated in our laboratories.[4] Th2-18 1F2 is the second thermal polymerization at $T = -18$ °C, first fractionation, fraction no. 2.

Solvents employed were p.a. grade from Merck, Darmstadt, except for *trans*-decalin, Merck, synthesis grade, which was distilled under vacuum prior to use, and technical grade THF, BASF, Ludwigshafen, which was distilled over metallic potassium.

Light-Scattering Measurements

In recent years the classical light-scattering technique has experienced a number of divergent evolutions based on improved technology as well as advanced theoretical treatment. In order to reduce the somewhat confusing and conflicting nomenclature employed in addressing the various light-scattering techniques, a new and unambiguous terminology based on the mode of evaluation is proposed: In classical light scattering for molecular weight determinations only the total intensity of the scattered light is measured, i.e., the time average over the intensities of all scattered frequencies. Therefore, this technique will be named frequency averaging (FAV) light scattering. When diffusion coefficients are determined by light

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[†] Dedicated to Professor P. J. Flory on the occasion of his 75th birthday.

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scattering, the frequency shift due to the motion of the molecules is examined; thus, the term frequency analyzing (FAN) light scattering is chosen for this technique.

As mentioned above, an accurate determination of M_w and radius of gyration $\langle S^2 \rangle_z^{1/2}$ (z average) requires that the reduced scattering intensity $R(\mu)$ be measured very precisely down to low scattering parameters $\mu = (4\pi/\lambda) \sin \theta/2$. Otherwise the scattering function $P(\mu)$ cannot be determined accurately enough for a precise extrapolation to $\mu = 0$. Any overlooked minor curvature in $P(\mu)$ at low μ will eventually lead to errors in the initial slope of $P(\mu)$ and the intercept, thus yielding an erroneous radius of gyration and molecular weight, respectively.

Most commonly, an increased accuracy is achieved by specially designed photometers,[3,8,12] allowing measurements down to low angles of θ at improved accuracy. Another possibility is to measure at various wavelengths up to the near IR, as was demonstrated by Meyerhoff and Burmeister.[13]

1. **Frequency Averaging Light Scattering.** For intensity determinations, two sets of measurements at widely different wavelengths (λ = 488 nm at T = 20 °C and λ = 1086 nm at 25 °C) and down to low scattering angles (θ = 9°) were carried out to ensure reliable results. The design and scope of the photometers have been described earlier,[8,12] and the same parameters were used as well.

Solutions of polystyrenes in toluene were prepared by diluting a stock solution and subsequent centrifugation in a table model centrifuge (Phywe A. G., Göttingen) for 0.5 h at 4700 gravity. The solutions and the solvent, subjected to the same procedure, were then pipetted into the scattering cells. It had been checked previously that during centrifugation under the above conditions no polymer was lost. The molecular weight from the test run was the same within experimental error as that obtained by the other methods employed here. Pipets and scattering cells had been made dust free by rinsing them with boiling acetone in an extraction column.

2. **Frequency Averaging Light Scattering with MWD Analysis.** With the recently available stable laser sources and electronic equipment, it is now possible to determine the scattering function $P(\mu)$ within an accuracy of 0.2–0.3%.[14] For the Schulz distribution of Gaussian coils, this scattering function has been calculated by Zimm[15] to

$$P(\mu) = \frac{2}{x^2}\left[x - (U+1) + (U+1)\left(1 + \frac{Ux}{U+1}\right)^{1/U}\right] \tag{1}$$

with $x = \mu^2 \langle S^2 \rangle_w$ and was modified into a more tractable form by Greschner[16]

$$P(\mu) = \frac{2}{(U+1)Y}[1 - Y^{-1} + Y^{-1}(1 + UY)^{-1/Y}] \tag{2}$$

with $Y = (\langle S^2 \rangle_z/[1 + 2U])\mu^2$. The accurately measured scattering function is approximated by a Gauss–Newton procedure by varying the three independent parameters M_w, $S_z = \langle S^2 \rangle_z^{1/2}$, and $U = M_w/M_n - 1$, where M_w and S_z are determined, as usual, from the intercept and the initial slope, respectively. The breadth of the distribution is obtained from the curvature of the scattering function, thus requiring the above mentioned accuracy in the light-scattering measurements (for a detailed description of this method see ref 14).

Measurements were carried out in *trans*-decahydronaphthalin at or near Θ conditions at a wavelength of λ = 632.8 nm (∂_n/∂_c = 0.1202 mL/g at T = 20 °C) covering 22 angles between 15° and 150°. Purification of the solutions was done in the same manner as above.

3. **Frequency Analyzing Light Scattering.** In the last years, FAN light scattering has become a standard technique for the determination of friction or diffusion coefficients.[17,18] In order to solely observe the motion of the center of mass, measurements have to be carried out at diminishing scattering parameters, especially for high molecular weight samples.

The homodyne photometer (λ = 514.5 nm) and evaluation procedure employed have been described earlier.[18] The solutions used were the same ones as for the conventional light scattering in toluene at T = 20 °C. The obtained diffusion coefficient is a z average as has been shown recently; higher orders of this average and the molecular weight distribution may be obtained as well.[19]

Ultracentrifuge Measurements

The ultracentrifuge provides a wide array of possibilities for the determinations of molecular weights on an absolute as well as on a relative scale; in addition to higher molecular weight averages, the entire MWD may also be obtained. Although there is virtually no limit in the determination, the procedures become more tedious and time consuming for the present range of interest.

Two practical absolute methods are available: equilibrium sedimentation and velocity sedimentation according to Svedberg[20] with separate determination of the diffusion coefficient. The former was ruled out because of the time requirements of up to 8 weeks for one run of an anionic polystyrene of $M_w = 44 \times 10^6$.[2] Thus the Svedberg method was chosen; additionally, it is a good starting point for two relative methods to determine the molecular weight and the MWD. All three methods are based on the same experimental technique but employ different evaluations.

1. **Svedberg Equation.** The sedimentation coefficient

$$s = \frac{\ln (r/r_0)}{\omega^2 t} f_p \tag{3}$$

at a given concentration was calculated by following the displacement of the maximum of the differential concentration profile as a function of time (ω is the angular velocity, r is the position of the maximum of the concentration gradient, r_0 is the position of the meniscus, and f_p is the pressure correction according to Meyerhoff).[21]

Subsequent extrapolation of these coefficients to zero concentration, c, according to

$$\frac{1}{s} = \frac{1}{s_0}(1 + k_s c) \tag{4}$$

yielded s_0 (concentration constant k_s). Thus with D_0 as obtained by FAN light scattering, $M_{s,D}$ can finally be computed with Svedberg's equation

$$M_{s,D} = \frac{s_0}{D_0} \frac{RT}{(1 - \rho v_2)} \tag{5}$$

(s_0 and D_0 are the sedimentation and diffusion coefficients, respectively, at infinite dilution; R is the gas constant; T is the temperature; ρ is the density of the solvent; and v_2 is the partial specific volume of the polymer).

2. **Molecular Weights on a Relative Scale.** s_0 may also be expressed as a simple function of the molecular weight

$$s_0 = K_s M^b \tag{6}$$

because a similar relation holds for D_0 as well ($D_0 = K_D M^{1-b}$). Once the constants K_s and b have been established by calibration with samples of known molecular weight, the evaluation is simple and straightforward.

3. MWD by Sedimentation. The polydispersity of a sample is reflected in the width of the sedimentation boundary. By looking at the entire boundary, a distribution of sedimentation coefficients $g(s)$ is therefore observed:[22,23]

$$g(s) = \mathrm{d}c/\mathrm{d}s = (\mathrm{d}c/\mathrm{d}r)(\mathrm{d}r/\mathrm{d}s)$$

which can be transformed into a MWD

$$w(M) = (\mathrm{d}s/\mathrm{d}M)(\mathrm{d}c/\mathrm{d}r)(\mathrm{d}r/\mathrm{d}s) \qquad (7)$$

with eq 4 and 6.

Experimentally one obtains an apparent MWD even while working under Θ conditions when the concentration dependence of s is strongly reduced. This apparent distribution has to be corrected for concentration and for broadening due to diffusion.[22,23] According to Pyun and Fixman,[24] the concentration dependence of the sedimentation coefficient is again a function of s_0 or M:

$$k_s = K_{sd}s_0^{\,d} \text{ or } k_s = K_{se}M^e \qquad (8)$$

(K_{sd}, K_{se}, d, and e are constants).

These relations can be established while obtaining the sedimentation coefficients, thus reducing the measurements of the MWD to one concentration. As has been shown (e.g., ref 25), the broadening of the concentration boundary due to diffusion is roughly proportional to the root of time, whereas the broadening due to polydispersity is proportional to time. Therefore, by extrapolating to infinite time, the diffusion dependence can be eliminated.[26] An extensive description (without the concentration correction) of this evaluation procedure is given by Cantow[22] and by McCormick.[23] Measurements were carried out in Spinco E centrifuges, Beckman, Palo Alto, Calif. Philpot-Svensson-Schlieren optics and standard aluminium cells were used for solutions of polystyrene in toluene (T = 20 °C) and in MEK (T = 25 °C). At very low concentrations, the standard cells were substituted by 30-mm cells. The UV absorption with scanner was employed for the cyclohexane solutions at T = 35 °C. At least six concentrations were prepared from the two separate stock solutions when s_0 was to be determined, and one ($c \le 2 \times 10^{-4}$ g/mL) solution was prepared for the MWD measurements in cyclohexane.

Viscometry

The viscometry, commonly appreciated as a tool because of its simplicity and ease, for samples of high molecular weight requires also a refined experimental technique to allow for the necessary velocity gradient measurements. In this work, a newly designed automated capillary viscometer was used which is based on fluid equilibration; the details have been described elsewhere.[10]

In each case at least six solutions were prepared and were purified by centrifuging in the same manner as for the light scattering. Measurements in toluene were carried out at T = 20 °C and in THF at T = 25 °C.

Gel Permeation Chromatography

GPC is probably the most convenient tool for investigating MWD's. It has to be established, however, that the spreading due to axial dispersion is negligable in order to use the "strip method" to evaluate the chromatograms; otherwise, tedious and time consuming correction procedures have to be utilized.

The chromatograph consisted of a Model A 6000 pump and a R401 differential refractometer (Waters, Assoc., Framingham). Alternatively, a UV detector ISCO-UV5 (Instrumentation Specialties Co., Lincoln, Neb.) was used at λ = 256 nm. The columns used were 3 × 7000, 3 × 6000, 1 × 5000 (Toyo Soda Mfg., Tokyo) and 1 × ($5 \times 10^4 - 1.5 \times 10^5$) (Waters Assoc., Framingham), in manufacturers notation. The flow rate of 1 mL/min of THF at 25 °C was measured with a drop counter. An amount of 1.25 mL of solution of less than 1.5 mg of polymer/mL was injected.

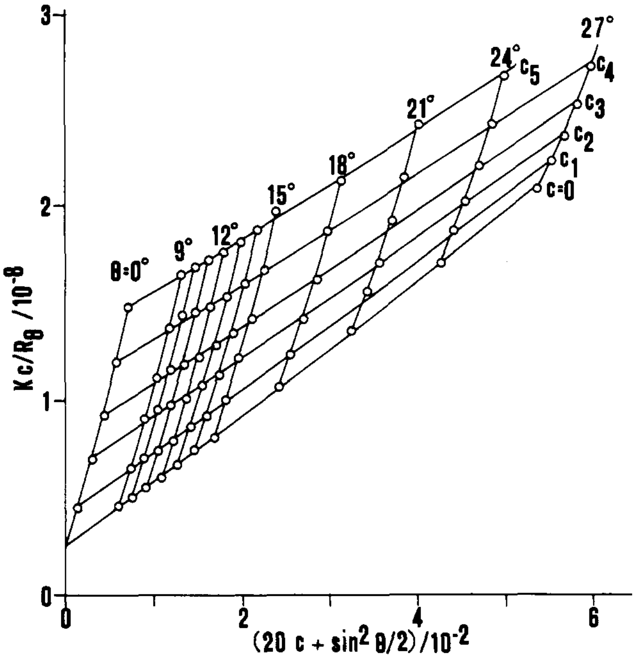

Figure 1. Zimm plot for Th2 -18 1F2 in toluene at 20 °C emphasizing low scattering angles. Concentrations are given in 10^{-4} g/mL: c_1 = 0.655, c_2 = 1.309, c_3 = 1.921, c_4 = 2.612, c_5 = 3.264.

Results and Discussion

The FAV (classical) light scattering results were evaluated by plotting the usual Zimm diagrams with the intercept yielding M_w, the initial slopes for zero concentration and for zero scattering angle yielding S_z and the virial coefficients, respectively. In Figure 1 such a Zimm plot is displayed for the low-angle range. This low-angle range was emphasized in these evaluations because a considerably higher scattering intensity is observed here as opposed to at higher angles. In addition, at higher angles reflection corrections have to be employed which may still involve some errors.

As can be seen from Figure 1, there are small yet distinct curvatures for both the concentration and the angle functions. The initial slope for the $P(\theta)$ function, and thus the radius of gyration, can still be evaluated easily from the initial slope either graphically or by a polynominal. The curvature for zero angle clearly indicates that, in addition to the second, the third virial coefficient has to be considered. This was done by substituting Flory's[27] empirical relation $A_3 = {}^1/_3A_2{}^2M_w$ into the Debye–Zimm equation, resulting in

$$\left(\frac{Kc}{R(\theta)}\right)^{1/2}_{\theta=0} = (1/M_w)^{1/2}(1 + M_wA_2c) \qquad (9)$$

The results, obtained by the two different photometers, are compared in Table I. The molecular weights, as well as the radii of gyration, agree within 5%, which is well within the accuracy of the two photometers. For the second virial coefficients (columns 3 and 9) the agreement of 15% is still reasonable; the difference in temperature of 5 °C has only a minor influence in the good solvent toluene. In columns 4 and 5, the virial coefficients as computed by eq 9 are reported and the A_2 in column 4 are

Table I
Results of Light-Scattering Measurements with Two Different Photometers for Polystyrene in Toluene

	λ = 488 nm, T = 20 °C						λ = 1086 nm, T = 25 °C[a]		
	M_w[b]	A_2[c]	A_2[c]	A_3[d]	$\langle S^2\rangle_z^{1/2}$[e]	U	M_w[b]	A_2[c]	$\langle S^2\rangle_z^{1/2}$[e]
Th2 -18 1F1	35.6	1.48	1.28	1.52	494	0.5	37.9	1.75	486
Th2 -18 1F2	40.2	1.37	1.12	1.65	515	0.2	39.3	1.52	496
Th2 -18 1F4	29.7	1.75	1.37	1.40	392	0.2			
Th2 -18 1F6	23.4	1.82	1.54	1.30	349	0.2			
Th2 -18 1F9	12.3	2.18	1.67	1.13	249	0.2			
Th2 -18	24.4	2.32			370	1.0	25.8	2.02	395
		slope	eq 9					slope	

[a] Reference 8. [b] 10^6 g/mol. [c] 10^{-4} (mL mol)/g². [d] 10^{-1} (mL² mol)/g³. [e] nm.

Table II
Weight Average Molecular Weights as Obtained from Classical Light-Scattering and Sedimentation and Diffusion Coefficients

	$M_{w,LS}$[a]	$s_{0,max}$[b]	$\langle s_0\rangle_w$[b]	$\langle D_0\rangle_z$[c]	$M_{w,sD}$[a]
Th2 -18 1F1	35.6	40.8	41.7	1.67	29.9
Th2 -18 1F2	40.2	47.6	48.1	1.43	40.3
Th2 -18 1F4	29.7	41.7	42.1	1.73	29.2
Th2 -18 1F6	23.4	37.0	37.4	2.02	22.2
Th2 -18 1F9	12.3	29.4	29.7	2.90	12.3

[a] 10^6 g/mol. [b] 10^{-13} s⁻¹. [c] 10^{-8} cm² s⁻¹.

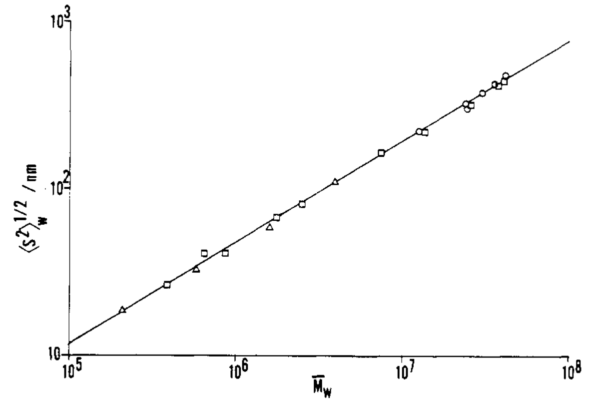

Figure 2. Weight average of radius of gyration $\langle S^2\rangle_w^{1/2}$ as a function of molecular weight for polystyrene in toluene: (○) this work, (□) A. Burmeister;[38] (△) H. Baumann.[36]

seen to be distinctly lower than the ones in column 3.

The radius of gyration, if corrected for the polydispersity according to $\langle S^2\rangle_w = \langle S^2\rangle_z(1 + U)/(1 + 2U)$,[28] may now be plotted as a function of molecular weight (Figure 2). It is clearly seen that within the experimental error, even up to these high molecular weights of 40 × 10⁶, a straight line is obtained: $\langle S^2\rangle_w^{1/2} = (1.107 \times 10^{-2})M^{0.605}$. Similar results for somewhat higher molecular weights have been reported for polystyrene in benzene at T = 25 °C.[3] Utiyama et al.[29] found a deviation from this behavior, which leads them to suggest a new empirical equation for the parameter z of the excluded volume effect.[30]

The virial coefficients are plotted as a function of the molecular weight as well. In both cases, straight lines may be used to represent the experimental results: $A_2 = (6.36 \times 10^{-3})M^{-0.225}$ and $A_3 = (2.56 \times 10^{-5})M^{0.502}$ (Figure 3).

The diffusion coefficients, obtained as a z average from the FAN light scattering, are listed in Table II and are plotted in Figure 4. Together with earlier data, the results are represented by the linear relation: $\langle D_0\rangle_z = (3.64 \times 10^{-4})M^{-0.577}$.

Some of the older data points are actually weight averages, but they fit the same relation well because they represent narrow samples.

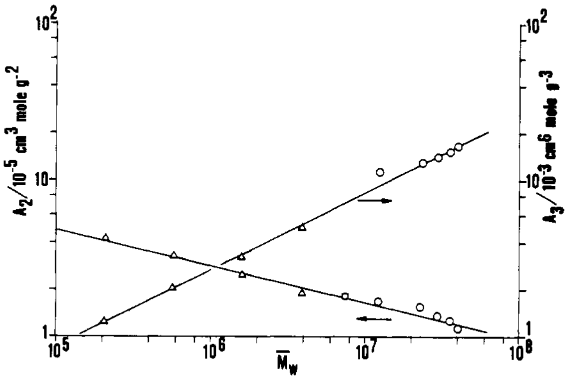

Figure 3. Second virial coefficient A_2 and third virial coefficient A_3 of polystyrene in toluene as a function of molecular weight: (○) this work; (□) A. Burmeister,[38] (△) H. Baumann.[36]

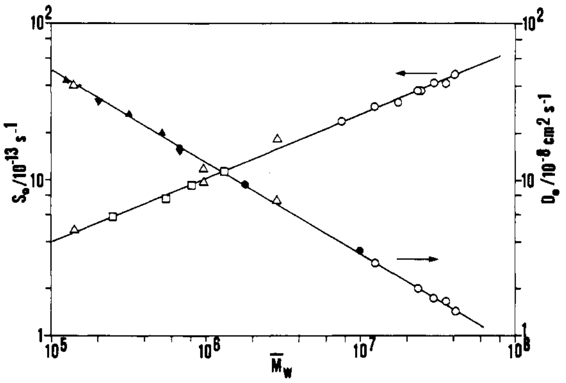

Figure 4. Sedimentation coefficient s_0 and diffusion coefficient D_0 as a function of molecular weight for polystyrene in toluene at 20 °C: (○) this work; (▲) G. Meyerhoff;[35] (△) K. Nachtigall;[39] (●) G. Büldt;[40] (□) S. Newman;[41] (▼) J. Raczek.[42]

The sedimentation coefficients for the same samples are listed in Table II as well. Since they were determined via Schlieren optics at the maximum of the boundary gradient, they are denoted as $s_{0,max}$. For a Schulz distribution, $s_{0,max}$ and $\langle s_0\rangle_w$ can be calculated and thus the following correction has to be applied:

$$\langle s_0\rangle_w = \frac{\Gamma(1/U + b + 1)}{\Gamma(1/U + 1)} \frac{s_{0,max}}{(1/U + 1 - b)^b} \quad (10)$$

with b from eq 6. Although the fractions definitely do not have a Schulz distribution, this has only a minor effect on the correction for narrow distributions. These corrections are necessary in order to calculate M_w from the Svedberg equation, which requires the $\langle s_0\rangle_w$ and $\langle D_0\rangle_z$ averages to be ratioed. In Table II, these $M_{w,sD}$ averages agree well with the molecular weights obtained by light scattering, showing again that the results are consistent with each other. The deviation for Th 2-18 1F1 may result from

Table III
Sedimentation Coefficients and Corresponding Concentration Coefficients for Polystyrene in Various Solvents[a]

sample	cyclohexane, $T = 35\ °C$		MEK, $T = 25\ °C$		toluene, $T = 20\ °C$	
	s_0[b]	k_s[c]	s_0[b]	k_s[c]	s_0[b]	k_s[c]
PCC 0.0048			1.75	19.2		
PCC 0.010			2.90	20		
PCC 0.020			4.12	−19		
PCC 0.037			5.04	0		
PCC 0.11			9.10	54		
PCC 0.20			11.9	90		
PCC 0.67	12.7	51.2	21.8	220		
TSK 2.4			35.4	322		
TSK 4.6	32.0	156				
TSK 7.5	40.0	138			23.8	1,670
TSK 9.6	47.1	188	64.7	843		
Th2 −18					36.4	3,930
Th2 −18 1F1					40.8	3,390
Th2 −18 1F2					47.6	4,670
Th2 −18 1F3					42.6	4,480
Th2 −18 1F4					41.7	4,430
Th2 −18 1F6					37.0	3.360
Th2 −18 1F7	60.8	203			31.3	2,740
Th2 −18 1F9					29.4	2.150
Th2 −18 1F10					25.9	1,940
Th2 −18 1F12					18.2	980

[a] Additional data used in eq 11a and 11c.[22,33–35]
[b] $10^{-13}\ s^{-1}$. [c] g/mL.

branching, since branched samples will exhibit smaller s_0 and D_0 values, and branched molecules will preferably accumulate in the first fraction of a precipitation fractionation.

At the same time, the above sedimentation coefficients, together with earlier results, are linearly dependent on the molecular weight in a double logarithmic plot (Figure 4). Further results from velocity sedimentation measurements, together with the concentration constants, are reported in Table III. Additional measurements in cyclohexane at $T = 35\ °C$ and in MEK at 25 °C are listed as well, resulting in the following relations:

toluene

$$T = 20\ °C \qquad \begin{aligned} s_0 &= (3.43 \times 10^{-2})M^{0.413} \\ k_s &= (8.08 \times 10^{-2})M^{0.74} \end{aligned} \tag{11a}$$

MEK

$$T = 25\ °C \qquad \begin{aligned} s_0 &= (4.62 \times 10^{-2})M^{0.452} \\ k_s &= (1.07 \times 10^{-1})M^{0.55} \end{aligned} \tag{11b}$$

cyclohexane

$$T = 35\ °C \qquad \begin{aligned} s_0 &= (1.46 \times 10^{-2})M^{0.501} \\ k_s &= (5.69 \times 10^{-2})M^{0.50} \end{aligned} \tag{11c}$$

The results from the viscometry are summarized in the two log–log linear relations which had been established for M_w up to 40×10^6 and had been reported earlier[10]

toluene

$$T = 20\ °C \qquad [\eta] = (1.069 \times 10^{-2})M^{0.724} \tag{12a}$$

THF

$$T = 25\ °C \qquad [\eta] = (1.363 \times 10^{-2})M^{0.714} \tag{12b}$$

All logarithmic relationships examined in this work, i.e., radius of gyration, diffusion coefficient, sedimentation coefficient, and viscosity number, are linear in molecular weight. Should there be a deviation from the linear behavior as occasionally has been suggested,[2,29] all relations should show some deviations, but, of course, to a different extent since their dependence on the radius of gyration is different in every case.

Now that it has been established that molecular weights of up to $M_w = 40 \times 10^6$ can reliably be determined, the results of the MWD analysis may also be discussed and are listed in Table IV. In many cases, the same samples were examined by several methods in order to check the consistency of the obtained values.

GPC is a well-established means of obtaining the distribution of a polymer, but the separation is usually limited for broad polymers to $M_w = 1.5 \times 10^6$. Newly available columns capable of separating higher molecular weight samples were selected with care to ensure a high resolution. Thus, it was possible to limit the instrumental spreading to an equivalent of $M_w/M_n = 1.02$ as determined from careful recalculation of calibration standards. In the case of small excess polydispersities, corrections of the MWD's according to Tung's equation can be omitted for broad polymers because such minor corrections have almost no effect on the final results.[31] The resolution of this GPC and the accuracy of the evaluations are demonstrated with the samples NBS 706 and Th 100, for which the MWD's are known. On this basis, the results for the other samples are seen to be reliable. Th 100 through Th 20 were also fitted to Schulz distributions with a coupling constant $k = 1/U = 1.0 \pm 0.1$. Higher molecular weight samples of broad MWD's could not be separated even at low concentrations causing occasional pressure increases or even column blocking, resulting in too small U values.

For the velocity sedimentation, the validity of the described procedure was tested with the same samples and equally good results were found (Table IV). The molecular weights of the samples Th 60, Th 40, and Th 20 compare well with those of the GPC results, but the polydispersity shows some discrepancy for Th 20. Th 60 and Th 40 could again be fitted to a Schulz distribution with a coupling constant of $k = 1.0 \pm 0.1$. All higher molecular weight samples show a rather low M_w/M_n, while a $M_w/M_n = 2$ is expected for thermal polystyrenes. Further varifying ex-

Table IV
M_w and M_w/M_n of Molecular Weight Distributions Resulting from Various Methods of Determination

sample	GPC		FAV light scattering		velocity sedimentation		fractionation	
	M_w[d]	M_w/M_n	M_w[d]	M_w/M_n	M_w[d]	M_w/M_n	M_w[d]	M_w/M_n
NBS 706	0.288	2.10	0.257[a]	2.10[a]	0.259	2.28		
Th 100	0.720	2.09			0.745	2.01	0.714[b]	2.20[b]
Th 60	1.69	1.98	1.64[c]	1.91[c]	1.91	1.89	1.80	1.92
Th 40	2.61	2.10			3.08	1.90	2.79	2.00
Th 20	4.79	2.33			5.14	1.61		
Th2 −18			24.4		21.9	1.84	22.1	1.98
Th3 −18			35.0[c]	2.21[c]	36.5	1.60		
Th4 −18			22.7[c]	1.72[c]	19.1	1.60		

[a] Standard polystyrene, No. 706, data from National Bureau of Standards. [b] Reference 37. [c] Reference 14. [d] 10^6 g/mol.

periments for these samples were therefore required.

FAV light scattering with an analysis of the $P(\theta)$ function has practically an operational range of $(0.5 \times 10^6)-(50 \times 10^6)$. Sample Th 60 was used to test the accuracy in obtaining the correct MWD; from column three, it is obvious that the agreement is good. The molecular weights of the other three samples agree well with those from velocity sedimentation, and the polydispersities are close to 2 as expected.

The final test for the presented results may be found in the last column where the values obtained by fractionation[4] are listed. Considering the diversities of all four methods of investigation, good agreement is found for M_w and M_w/M_n of the Th 60. The further agreements and some diversities of the results for the other samples, therefore, serve as an outline of the regions to which the various procedures may be employed. The upper limit of GPC analysis for broad distribution polystyrenes has now been extended to about $M_w = 5 \times 10^6$. For velocity sedimentation, the limit for determining the distribution is presently at about $M_w = 3 \times 10^6$, whereas for the molecular weights as such, no apparent limit is seen.[32] The working range of the FAV (classical) light scattering, on the other hand, conveniently starts at about $M_w = 0.5 \times 10^6$ and extends to at least $M_w = 50 \times 10^6$. These three methods therefore compliment each other in their range of applicability, covering the entire range of molecular weights which is also accessible to fractionation. At the same time, GPC, sedimentation, and light scattering have the definite advantages of being quick and easy to perform as opposed to fractionation.

Conclusions

It has been shown that FAV light scattering and Svedberg's method can be correctly used to determine molecular weights on an absolute scale up to $M_w = 40 \times 10^6$. By velocity sedimentation (sedimentation coefficient), FAN light scattering (diffusion coefficient), and viscometry, relative molecular weight may be determined over the same range. All determined quantities proved to be linear functions of the molecular weight in double logarithmic plots. Further, MWD's of M_w up to 5×10^6 can be determined by GPC, 3×10^6 by velocity sedimentation, and at least 35×10^6 by light scattering, thus extending the reliable working range of the above-mentioned methods of investigation to new limits.

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