Flory's Viscosity Factor for the System Polystyrene + Cyclohexane at 34.5 °C

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ABSTRACT: Two nearly monodisperse samples of polystyrene ($M_w \sim 6.5 \times 10^6$, $M_w/M_n < 1.05$, $M_z/M_w < 1.03$) were prepared by extensive fractionation of a standard sample, and their light-scattering envelopes and intrinsic viscosities in cyclohexane at 34.5 °C, chosen as the Θ solvent, were measured with great care. From the data obtained, Flory's viscosity factor Φ free from polydispersity effects was estimated to be $(2.5_5 \pm 0.1) \times 10^{23}$ mol^{-1}. This is 10% smaller than the asymptotic value 2.87×10^{23} mol^{-1} predicted with the preaveraged Oseen tensor for an unperturbed linear polymer.

Flory's viscosity factor Φ is defined by the relation[1]

$$[\eta] = 6^{3/2}\Phi(\langle S^2\rangle/M)^{3/2}M^{1/2} \qquad (1)$$

where $[\eta]$ and $\langle S^2\rangle$ denote, respectively, the intrinsic viscosity and mean-square radius of gyration of a monodisperse polymer with molecular weight M in a solvent. According to the vast amount of experimental results, this factor is essentially independent of M and solvent species for a series of homologous linear polymers in a Θ solvent. This general feature of Φ for unperturbed linear polymers has become the object of many theoretical studies, but no exact evaluation of Φ is as yet achieved. As is well known, the difficulty in attempting the calculation of Φ for flexible polymers lies in the treatment of the Oseen tensor for hydrodynamic interactions between chain segments. If this tensor is averaged over the chain conformation prior to the computation of $[\eta]$, we find for the unperturbed Gaussian chain that Φ tends asymptotically to the value 2.87×10^{23} mol^{-1} as M is increased.[2] Attempts to estimate the effects of preaveraging the Oseen tensor were made by Pyun and Fixman[3] and later by Bixon and Zwanzig.[4] Thus the former obtained 2.66×10^{23} mol^{-1} and the latter 2.76×10^{23} mol^{-1} as the asymptotic value of Φ for the Gaussian chain. Because of the complicated analyses used, it is difficult to estimate the accuracy of these results, but it seems certain that the exact theoretical Φ will be found somewhat below the preaveraged value.

Most experimental values of Φ for linear flexible polymers in Θ solvents are, in fact, comparable to but almost consistently lower than these theoretical values. This is illustrated in Table I by presenting the Φ values for polystyrene in two Θ solvents calculated from the original data given in some typical papers. We note that the indicated values are not corrected for polydispersity effects on $\langle S^2\rangle$ and $[\eta]$. The scatter and disagreement of Φ values reported on the same system by different authors is generally as much as can be seen in Table I, and it is usually attributed to the difference in polydispersity of the polymer fractions used for the measurements, but the difficulty in accurate light-scattering determination of $\langle S^2\rangle$ cannot be overlooked as its serious cause. In the experimental evaluation of Φ, it is crucial to correct measured values of z-average mean-square radius of gyration $\langle S^2\rangle_z$ for the polydispersity effect. Some authors did this correction assuming a suitable form, e.g., the Schulz–Zimm exponential function, for the molecular weight distribution. However, in our opionion, the use of such an approximation is never desirable.

This paper reports our attempt to approach the correct value of Φ for monodisperse polystyrene in cyclohexane at 34.5 °C, the Θ temperature for this polymer + solvent system. For this purpose, we prepared very narrow-distribution samples from a commercial "monodisperse" polystyrene and carried out all the necessary measurements with great care.

Table I
Typical Experimental Values of Φ for Polystyrene

authors	Θ solvents	$M_w \times 10^{-6}$/ g mol^{-1}	$\Phi \times 10^{-23}$ [i]/ mol^{-1}
Krigbaum-Carpenter[a]	cyclohexane	3.2	1.85
McIntyre et al.[b]	cyclohexane, 35 °C	4.0	1.76
Berry[c]	decalins	0.62-4.4	1.7-2.6
	cyclohexane, 34.8 °C	0.62-1.6	2.6-2.9
Cowie-Cussler[d]	cyclohexane, 35 °C	0.21-1.0	1.7-2.1
Yamamoto et al.[e]	cyclohexane, 34.6 °C	0.34-2.9	2.4-2.6
McIntyre et al.[f]	cyclohexane, 35.4 °C	27-44	1.5-2.0
Fukuda et al.[g]	*trans*-decalin, 20.4 °C	1.2-4.6	2.2-2.8
Einaga et al.[h]	cyclohexane, 34.5 °C	8.8-57	2.2-2.4

[a] W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, 59, 1166 (1955). [b] D. McIntyre, A. Wims, L. C. Williams, and L. Mandelkern, *J. Phys. Chem.*, 66, 1932 (1962). [c] G. C. Berry, *J. Chem. Phys.*, 44, 4550 (1966); 46, 1338 (1967). [d] J. M. G. Cowie and E. L. Cussler, *J. Chem. Phys.*, 46, 4886 (1967). [e] A. Yamamoto, M. Fujii, G. Tanaka, and H. Yamakawa, *Polym. J.*, 2, 799 (1971). [f] D. McIntyre, L. J. Fetters, and E. Slagowski, *Science*, 176, 1041 (1972). [g] M. Fukuda, M. Fukutomi, Y. Kato, and H. Hashimoto, *J. Polym. Sci., Polym. Phys. Ed.*, 12, 871 (1974). [h] Y. Miyaki, Y. Einaga, and H. Fujita, *Macromolecules*, 11, 1180 (1978); Y. Einaga, Y. Miyaki, and H. Fujita, *J. Polym. Sci., Polym. Phys. Ed.*, 17, 2103 (1979). [i] Uncorrected for polydispersity.

Experimental Section

Polymer Samples. On our previous experiences we chose Toyo Soda's standard polystyrene F550 with an M_w of about 6.0×10^6 as the starting material. Curve A in Figure 1 shows its GPC diagram; the curve gives 1.14 for the M_w/M_n ratio if the calibration line of the apparatus shown in Figure 2 is used. Sample F550 was fractionated in the following way to extract narrower-distribution samples.

First, the sample was divided into three parts by precipitating it successively from a cyclohexane solution of concentration 7.6×10^{-4} g cm^{-3} by lowering the temperature in a stepwise fashion.

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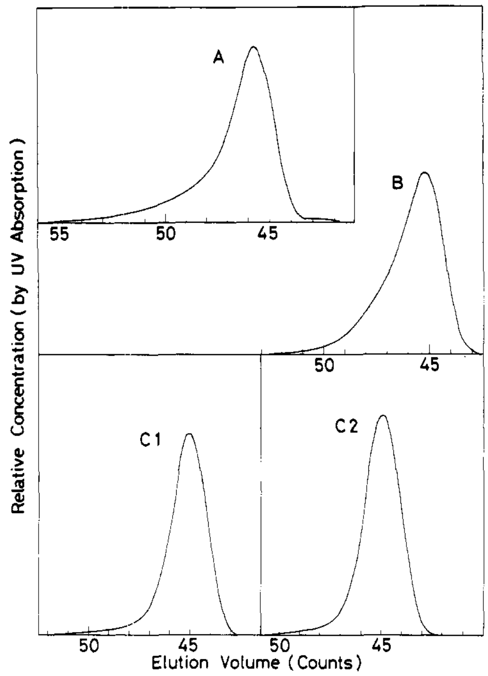

Figure 1. GPC diagrams: A, for original sample F550; B, for sample B22 from fractional precipitation; C1 and C2, for samples C1 and C2 from fractional precipitation and column elution.

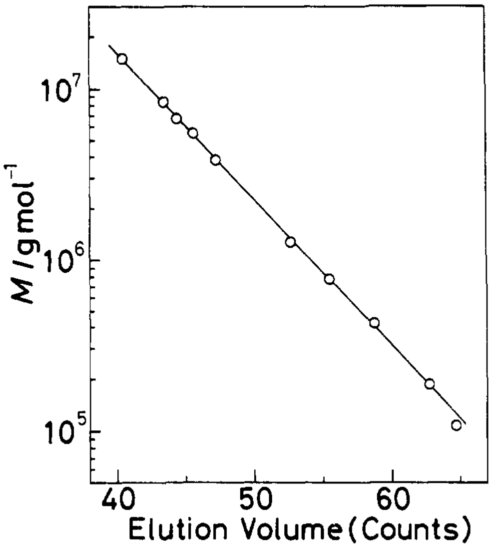

Figure 2. Calibration curve of the GPC instrument, determined by the usual peak method with Toyo Soda's standard polystyrene samples.

The middle fraction was again divided into three parts by the same method, this time the initial concentration being adjusted to 5.5×10^{-4} g cm^{-3}. Curve B in Figure 1 shows the GPC diagram of the middle fraction (designated B22) from the second fractionation. If this curve is compared with curve A, we find that the high-molecular-weight tail in sample F550 was eliminated.

To remove the low-molecular-weight tail of curve B, sample B22 was subjected to column elution. A cyclohexane solution of B22 was mixed with fine glass beads, and the mixture was packed in a column at 40 °C. The polymer was then allowed to precipitate on the glass beads by lowering the temperature to about 28 °C. The temperature was raised stepwise for successive elutions, and ten fractions were recovered, one at each specified temperature. The ninth fraction (0.43 g) was treated in a similar way, and the fourth and the fifth fractions (0.097 and 0.059 g, respectively) of the six fractions obtained were taken as the samples for the present study. They are designated C1 and C2 in the ensuing description.

Curves C1 and C2 in Figure 1 are the GPC diagrams of these fractions, indicating that the column fractionation was effective in removing the low-molecular-weight tail of the GPC curve of sample B22. The polydispersity indices computed from these curves (Table II) suggest that both samples C1 and C2 are nearly monodisperse and presumably meet the aim of the present investigation.

Table II
Polydispersity Indices of Samples C1 and C2 as Estimated from GPC Curves

samples	M_w/M_n	M_z/M_w	$M_w^{0.5}/(M^{0.5})_w$
C1	1.0_6	1.0_4	1.00_6
C2	1.0_5	1.0_4	1.00_5

Before use, either C1 or C2 was reprecipitated into methanol from a benzene solution and dried at 50 °C under reduced pressure for 4 days. It was confirmed by GPC that the benzene used for the reprecipitation had evaporated out of the sample during the drying process.

A Toyo Soda's HLC802UR, equipped with four G6000H6 columns in series (about 250 cm long), was used for the GPC measurements. The solvent was tetrahydrofuran, the initial polymer concentration 0.02 wt.%, the sample 0.5 cm^3, and the flow rate 1 cm^3 min^{-1}. The theoretical plate number of the instrument for acetone was about 50000. The molecular weight vs. elution volume relation shown in Figure 2 was determined with a series of Toyo Soda's standard polystyrene samples.

Preparation of Solutions. Each sample was dissolved in cyclohexane at 40 °C by allowing the mixture to stand in the dark for 1 week and then shaking it gently for 1 day. No mechanical stirring was applied. The solution was diluted with the solvent to the desired concentrations. Before use for a light-scattering measurement, each of the test solutions, placed in a 15-cm^3 Pyrex tube with a Teflon ground stopper, was centrifuged at 19000 times gravity for 2 h. The supernatant was carefully transferred into the light-scattering cell with a pipet. Both the cell and pipet were cleaned by refluxing acetone vapor. All these operations were carried out so that the solution was never cooled below 40 °C.

Light-Scattering Measurement. A Fica 50 photogoniometer was used, together with the experimental techniques tested and improved repeatedly in our laboratory over more than a decade. The optical alignment of the instrument was made in such a way that the volume-corrected intensity ratio $I(\theta) \sin \theta / I(90°)$ did not deviate more than ±0.005 from unity in the range of scattering angle θ from 15 to 150° when vertically polarized light was incident to an aqueous solution of fluorescein of concentration 4×10^{-7} g cm^{-3}. The instrument was calibrated by the usual method with pure benzene as the reference liquid. The following literature values[5] were used for Rayleigh's ratios of pure benzene at 25 °C for unpolarized light: 46.5×10^{-6} cm^{-1} for wavelength 436 nm and 16.1×10^{-6} cm^{-1} for wavelength 546 nm. The depolarization ratio of pure benzene was estimated by the method of Rubingh and Yu;[6] it was 0.41 for 436 nm and 0.40 for 546 nm.

With vertically polarized light as the incident beam, the intensity of light scattered from a test solution was measured at scattering angles from 30 to 150° for wavelength 436 nm and from 22.5 to 150° for wavelength 546 nm. For sample C1 the experiment was repeated three times on an independently prepared series of solutions to check the reproducibility of the results, but for sample C2 only one series of solutions was examined. These experiments on cyclohexane solutions were done at 34.5 °C. Sample C1 was also examined in benzene at 25 °C.

Measurement of Refractive Index Increment. The specific refractive index increment $\partial n/\partial c$ of polystyrene in cyclohexane at 34.5 °C was determined in a modified Schulz–Cantow differential refractometer calibrated with Kruis' data on aqueous KCl as the reference.[7] To save samples C1 and C2 for other measurements, a fraction of $M_w = 18.4 \times 10^4$ extracted from Toyo Soda's standard polystyrene F20 was used. The measured excess refractive index values Δn are plotted against polymer mass concentration c in Figure 3. The slopes of the straight lines, equated to $\partial n/\partial c$, are 0.181 ± 0.001 cm^3 g^{-1} for wavelength 436 nm and 0.171 ± 0.001 cm^3 g^{-1} for wavelength 546 nm. Bodmann's value[8] was assumed for $\partial n/\partial c$ of polystyrene in benzene at 25 °C.

Viscosity Measurement. Our previous study[9] on ultrahigh molecular weight polystyrene suggested that the intrinsic viscosity

Table III
Results from Light-Scattering and Viscosity Measurements

systems	M_w/ 10^6 g/mol	$\langle S^2\rangle_{0z}^{0.5}$/ 10^{-8} cm	$\langle S^2\rangle_0/M$/ 10^{-18} cm^2 mol/g	M_w/M_n	M_z/M_w	$[\eta]_\theta$/ 10^2 cm^3/g	Φ^*/ 10^{23} mol^{-1}
C1 + benzene, 25 °C	6.4_9	1350					
C1 + cyclohexane, 34.5 °C							
expt No. 1	6.4_8	74_1	8.2_4	1.0_4	1.03	2.28	2.5_8
expt No. 2	6.4_1	74_2	8.4_1	1.0_5	1.01		2.5_1
expt No. 3	6.5_0	73_8	8.2_3	1.0_0	1.02		2.5_8
C2 + cyclohexane, 34.5 °C	6.5_5	74_6	8.3_7	1.0_3	1.02	2.30	2.5_3

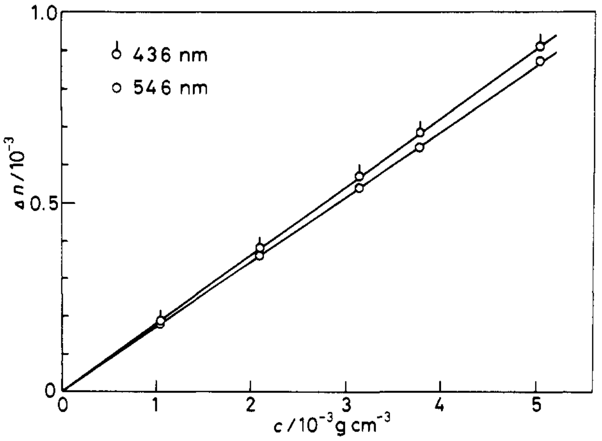

Figure 3. Plots for excess refractive index Δn vs. mass concentration c of polystyrene in cyclohexane at 34.5 °C.

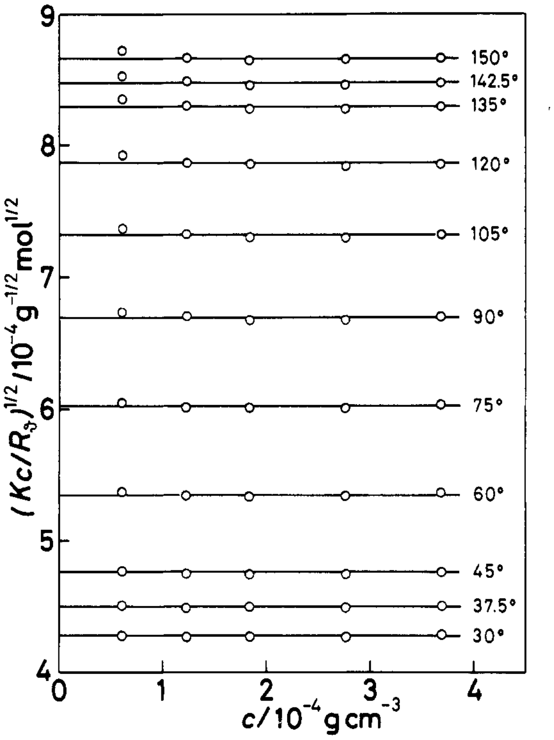

Figure 4. Plots of the reciprocal square root of reduced scattering intensity $(Kc/R_\theta)^{1/2}$ vs. polymer mass concentration c for sample C2 in cyclohexane at 34.5 °C; the wavelength of the incident beam is 436 nm.

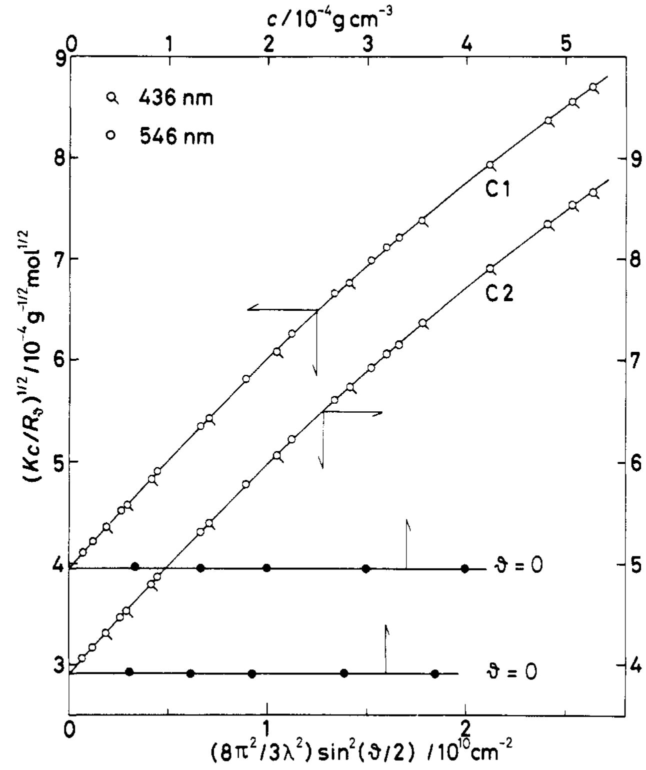

Figure 5. Plots of zero-angle $(Kc/R_\theta)^{1/2}$ vs. c and infinite-dilution $(Kc/R_\theta)^{1/2}$ vs. $(8\pi^2/3\lambda^2)\sin^2(\theta/2)$ for samples C1 and C2 in cyclohexane at 34.5 °C.

of polystyrene in cyclohexane at 34.5 °C should suffer no shear rate effect if the molecular weight is lower than 10^7. For sureness, however, flow times were measured in the two central bulbs of the previously described capillary viscometer of a spiral type.[9] In no case was the shear rate dependence of the flow time detected within experimental errors. The solvent flow times for the two bulbs were so large that an accurate determination of the specific viscosity η_{sp} could be made down to about 0.05. For sample C1 two series of solutions were prepared independently and subjected to the measurement.

Results and Discussion

Light Scattering. By way of example, the light-scattering data on sample C2 in cyclohexane at 34.5 °C are illustrated in Figure 4, in which K is the well-known optical constant involving $(\partial n/\partial c)^2$, R_θ is the reduced scattering intensity at a scattering angle Θ, and c is the polymer mass concentration. Except for a few points at the lowest concentration, the data points at each scattering angle can be fitted by a horizontal line. This fact indicates that the second virial coefficient of the system polystyrene + cyclohexane vanishes at 34.5 °C, as has been confirmed repeatedly by previous authors.

Figure 5 shows the infinite-dilution and zero-angle scattering envelopes for the two samples, displayed in the form of Berry's square-root plot.[10] Here λ denotes the wavelength of the incident beam in the solution. The plotted points for sample C1 refer to experiment No. 2. The corresponding data from experiments No. 1 and No. 3 were indistinguishable from these. The values of weight-average molecular weight M_w and unperturbed z-average mean-square raidus of gyration $\langle S^2\rangle_{0z}$ determined by the usual method from Figure 5 and similar graphs for experiments No. 1 and No. 3 are presented in

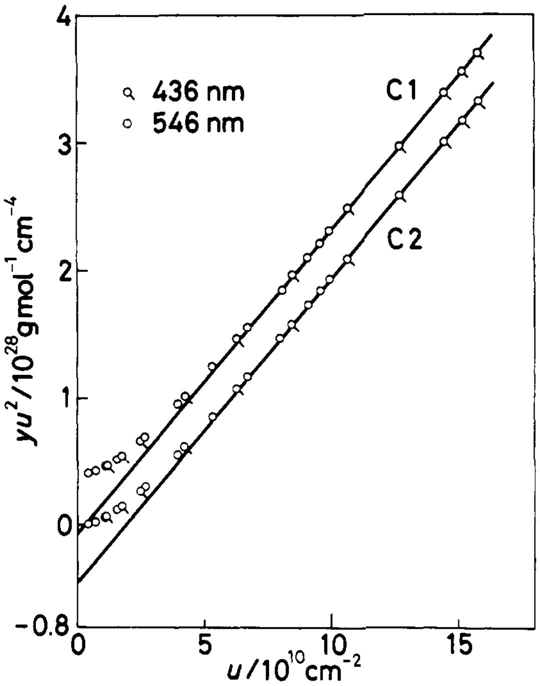

Figure 6. Plots of yu^2 vs. u for samples C1 and C2 in cyclohexane at 34.5 °C. The data points for sample C1 are displaced upward by 0.4×10^{28}. The solid lines indicate the asympotes. See the text for the definition of y and u.

the second and third columns of Table III. It is seen that the three independent experiments on sample C1 yielded very consistent values for both M_w and $\langle S^2\rangle_{0z}$ and that the measurements on benzene and cyclohexane solutions of sample C1 led to essentially the same values of M_w. These results indicate something about the precision of our light-scattering experiment.

In principle, the characteristic ratio $\langle S^2\rangle_0/M$ of an unperturbed monodisperse linear polymer can be estimated by the "asymptote" method from the infinite-dilution scattering envelope of a polydisperse sample in a Θ solvent if the sample is sufficiently high in M_w and narrow in molecular weight distribution. These conditions on the sample are necessary, because otherwise the asymptote does not appear in the region of scattering angle accessible to experiment. Probably for the first time we observed the asymptote clearly in our recent study on ultrahigh molecular weight samples of polystyrene.[11]

We now show that the scattering envelopes displayed in Figure 5 can be analyzed by the "asymptote" method. Figure 6 shows the yu^2 vs. u plots derived from these envelopes, where y and u denote $(R_\theta/Kc)_{c=0}$ and $(4\pi/\lambda)^2 \sin^2(\Theta/2)$, respectively. It is seen that the plot for either sample exhibits a linear region for u above 9×10^{10}. This region can be taken as the asymptote in question, which is represented by the relation[11]

$$yu^2 = -\frac{2}{M_n}\left(\frac{M}{\langle S^2\rangle_0}\right)^2 + 2\frac{M}{\langle S^2\rangle_0}u \qquad (2)$$

Thus the asymptote allows not only the desired characteristic ratio $\langle S^2\rangle_0/M$ but also the number-average molecular weight M_n of the sample to be determined from its slope and intercept. Once $\langle S^2\rangle_0/M$ is known, the z-average molecular weight M_z can be calculated from the $\langle S^2\rangle_{0z}$ value (determined from the initial slope of the infinite-dilution scattering envelope), since the relation $M_z = \langle S^2\rangle_{0z}(\langle S^2\rangle_0/M)^{-1}$ holds.

The results derived by analyzing our light-scattering data in terms of eq 2 are presented in the fourth, fifth, and sixth columns of Table III. Here the values of M_w/M_n and M_z/M_w, rather than those of M_n and M_z themselves, are shown in order to indicate the heterogeneity of each sample. Of these results, the M_w/M_n values are least accurate, because M_n had to be estimated from relatively small intercepts of the asymptotes. On the other hand, the M_z/M_w values are considered quite accurate. They are very close to unity, in fact even more so than the values estimated from the GPC curves (see Table II). It is to be noted that the derivation of these values of M_w/M_n and M_z/M_w involves no assumption for the molecular weight destribution; the only condition is that the particle scattering function of an unperturbed monodisperse linear polymer should obey the Debye function for the Gaussian chain.[12] The values obtained for the characteristic ratio $\langle S^2\rangle_0/M$ give $8.3_1 \times 10^{-18}$ cm^2 mol g^{-1} as the arithmetic average. This is in substantial agreement with the average $8.3_5 \times 10^{-18}$ cm^2 mol g^{-1} reported in our previous paper on ultrahigh molecular weight polystyrene samples.[11]

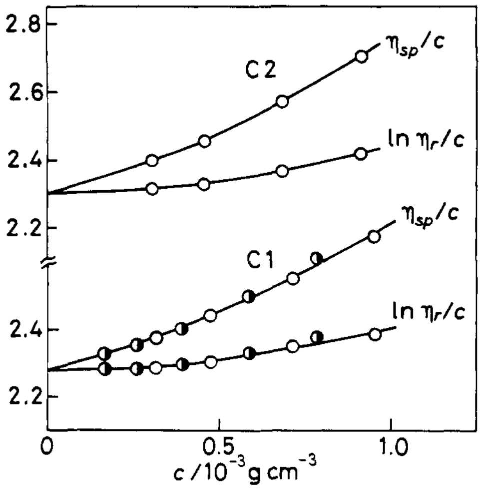

Figure 7. Huggins' and Fuoss–Mead's viscosity plots for samples C1 and C2 in cyclohexane at 34.5 °C. The ordinate is given in units of 10^2 cm^3 g^{-1}. Different marks for sample C1 indicate independent measurements.

Viscosity. The results from the viscosity measurements are shown in Figure 7 as plots of η_{sp}/c and $(\ln \eta_r)/c$ against c, where η_r denotes the relative viscosity of the solution. The intrinsic viscosities $[\eta]_\theta$ determined from these plots are presented in the seventh column of Table III. Since no shear-rate effect was observed, these values may be considered to represent $[\eta]_\theta$ at the zero shear rate.

Flory's Viscosity Factor. With the numerical results presented in Table III, we can evaluate an apparent Flory viscosity factor Φ^* defined by the relation

$$[\eta]_\theta = 6^{3/2}\Phi^*(\langle S^2\rangle_0/M)^{3/2}M_w^{1/2} \qquad (3)$$

The computed values are given in the last column of Table III. The definition of Φ^* differs from the usual apparent Flory viscosity factor in the point that the characteristic ratio $\langle S^2\rangle/M$ is not replaced by $\langle S^2\rangle_z/M_w$. Thus, Φ^* is free from the polydispersity effect on the characteristic ratio. If, as is usually postulated, the intrinsic viscosity $[\eta]_{\theta m}$ of an unperturbed monodisperse linear polymer is strictly proportional to $M^{1/2}$, it follows that $[\eta]_\theta/M_w^{1/2}$ is equal to $K(M^{1/2})_w/M_w^{1/2}$, where K is the proportionality factor between $[\eta]_{\theta m}$ and $M^{1/2}$ and $(M^{1/2})_w$ is the weight average of $M^{1/2}$. With these relations, we obtain from eq 1 and 3

$$\Phi/\Phi^* = M_w^{1/2}/(M^{1/2})_w \qquad (4)$$

The values of the right-hand side computed from the GPC curves C1 and C2 do not exceed 1.01 (see Table II). Thus we may conclude that the value of Flory's viscosity factor

Φ for monodisperse polystyrene in cyclohexane at 34.5 °C is

$$\Phi = (2.5_5 \pm 0.1) \times 10^{23}\ \mathrm{mol}^{-1}$$

where the value 0.1 represents a rough estimate of the total uncertainty associated with our measurements and data analysis. This final value is smaller than the three theoretical values quoted at the beginning of this paper. The disagreement can no longer be attributed to the polydispersity effect. It is our great pleasure to quote Flory's statement[13] that, "the true value (of Φ) probably is about 2.5×10^{21} in the previously given units" (which corresponds to 2.5×10^{23} mol^{-1}).

The absolute value of our Φ depends on the literature values chosen for Rayleigh's ratio for pure benzene and the specific refractive index increment of aqueous KCl in calibrating our photogoniometer and differential refractometer, respectively. We simply accepted them as correct, since in no case of our previous studies on a variety of polymer + solvent systems had we met any significant and systematic disagreement between the M_w values determined by light scattering with these literature data and those by sedimentation equilibrium.

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Chain Molecule Hydrodynamics by the Monte-Carlo Method and the Validity of the Kirkwood–Riseman Approximation

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ABSTRACT: A preaveraged hydrodynamic interaction between chain segments was introduced by Kirkwood and Riseman in their well-known 1948 paper on sedimentation and viscosity, but its degree of correctness for chain molecules has never been well established. In this paper we avoid the approximation by creating a number of randomly generated chain configurations on a computer, solving the Burgers–Oseen interaction problem for each configuration, and finally averaging the results, thus getting rid of the preaveraging approximation. A chain model of beads with Gaussianly distributed spacing was used. Two thousand Gaussianly distributed interbead vectors were created by a pseudo-random-number generator, and these were strung together end-to-end in various ways into chains of up to 50 vectors per chain. Each 50-vector chain required the solution of 157 simultaneous equations. The results for the 50-vector chain show that the Kirkwood–Riseman (KR) sedimentation coefficient is about 13% too high, the KR intrinsic viscosity is about 12% too high, and the molecular weight calculated by the Flory–Scheraga–Mandelkern formula from the combination of sedimentation and viscosity is about 25% too low. Comparison of chains with 5, 10, 25, and 50 vectors suggests that a chain with an infinite number of beads would not give results much different from the 50-vector case.

We consider the effects of two approximations introduced into the theory of the hydrodynamic properties of chain molecules by Kirkwood and Riseman[1] and by Kirkwood.[2] The first of these approximations consisted of preaveraging the hydrodynamic interactions between the segments of the chain and the second of approximating the inverse of the diffusion tensor by the tensor composed of the inverses of the elements of the original tensor. These approximations have been discussed, and improved or removed in some special cases, by subsequent authors.[3-7] Here we shall attempt to assess by numerical "Monte-Carlo" methods the effects of these approximations on the sedimentation coefficient and on the viscosity number (intrinsic viscosity). Another objective is to improve the determination of the molecular weight by the Flory–Scheraga–Mandelkern method from viscosity and sedimentation.

The model is a random-flights chain constructed from N vectors of random length and direction joined end to end. As usual, the vectors connect $N + 1$ segments each with Stokes radius a. A number of such chains with different conformations are generated, and the hydrodynamic problem is solved for each chain; the results are then averaged. In this way the preaveraging of the Kirkwood–Riseman (KR) approximation is avoided; at the same time the inverses are taken in the correct order.

Methods

We replace the real system of flexible chain molecules by an ensemble of rigid, randomly selected models of chains. While this procedure appears to be a drastic oversimplification, we attempt to show below that it is valid as long as Brownian motion is overwhelming.

Consider an ensemble of molecules in a certain steady state with applied external forces or external flows. In steady state the system is translating (in sedimentation) or rotating (in laminar flow) at a constant rate, while the distribution of internal coordinates (exclusive of orientation

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