Diffusion of polystyrene in tetrahydrofuran

W. Mandema and H. Zeldenrust
Koninklijke/Shell-Laboratorium, Amsterdam, Netherlands

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The diffusion of polystyrene in tetrahydrofuran has been studied by line width measurements in a laser light scattering spectrometer. The diffusion coefficient D has been determined as a function of concentration c for the molecular weight range of 2.04×10^4 to 1.8×10^6. At low concentration the relationship between D and c is linear to a very good approximation over a relatively large concentration region, as has also been found for some other systems. The molecular weight dependence of D, extrapolated to zero concentration, D_0 can be written as $D_0 = k_T \bar{M}_w^{-b}$, where $b = 0.564$, in good agreement with thermodynamic predictions derived from intrinsic viscosity studies.

INTRODUCTION

During the last few years increasing interest has arisen in the diffusional behaviour of macromolecules in solution. Experimental work in particular has been highly stimulated by the development of a new measuring technique, which is also used here: laser light beating spectroscopy. This method, amply reviewed in the literature[1–3], is based on the analysis of the Doppler broadened spectrum of scattered light and has proven to be a very fast and reliable tool for obtaining accurate values for the diffusion coefficient of macromolecules.

The free diffusion of a macromolecule in solution depends on both thermodynamic and hydrodynamic polymer–solvent interactions. The thermally excited concentration fluctuations are the driving forces for the diffusion process, which is opposed by the frictional forces exerted by the molecular surroundings. Both types of interaction depend on the solute concentration c. The relationship between the diffusion coefficient D and c is commonly written in a series expansion of the form:

$$D = D_0(1 + k_D c + \dots) \qquad (1)$$

where D_0 is the diffusion coefficient at infinite dilution. This concentration dependence of D has been the subject of a large number of experimental and theoretical investigations, but there exist striking differences between the various results with regard to the concentration region within which equation (1) can be approximated by the first two terms and higher terms can be neglected (linear approximation). For instance, using polarization interferometry Tsvetkov and Klenin[4] found, in a thorough study of the diffusion of polystyrene in tetrachloromethane and butanone, a rather complicated behaviour with a concentration-independent region at very low concentrations. Other investigators[5–9] did not observe this type of behaviour, but their measurements also disagree in many respects with each other. Moreover, lack of sufficient accurate experimental data makes it difficult to verify the validity of the existing theoretical expressions[10–12] for the coefficient of the linear term in equation (1), k_D.

In this work we present experimental data of the diffusion of polystyrene in the good solvent tetrahydrofuran (THF) as a function of concentration and molecular weight, from which reliable values of the parameter k_D could be obtained. The results show a relatively large concentration region where D varies linearly with c, confirming the work of King *et al.*[7,8] and of Pusey *et al.*[9] on comparable systems.

EXPERIMENTAL

The basic arrangement of the light beating spectrometer is the same as that of some others described in literature[1–3]. The spectrometer in essence resolves the line width of the optical spectrum of scattered light by homodyning at the photomultiplier and analysing the resulting photocurrent by measurement of its autocorrelation function. The light source is an ion laser (Spectra Physics, model 165) provided initially with a krypton plasma tube and later on with an argon tube. Scattered light is collected with an angular acceptance of 0.1° and detected by an EMI 9558 QB photomultiplier tube. The photocurrent is analysed by a Hewlett–Packard correlator, model 3721 A.

In the present case the detectable part of the optical spectrum is merely determined by a symmetric, diffusional broadening caused by the random motions of the scatterers, the solute macromolecules. Then the computed correlation function is, apart from a sharp shot noise peak at time $\tau = 0$, an exponential whose characteristic time τ_c is related to the translational diffusion coefficient D according to:

$$1/\tau_c = \frac{32\pi^2}{\lambda^2} \sin^2 \vartheta/2 \times D \qquad (2)$$

where λ is the wavelength in the medium and ϑ is the scattering angle.

For all experiments the relevant part of the correlation function was found to be given by one single exponential and the angular dependence of τ_c as predicted by equation (2). Evidently, the translational diffusion was indeed the only cause of the line broadening. The final diffusion coefficient has been calculated by averaging individual values obtained for at least four scattering angles, usually at 20, 25, 30 and 45°. The observed standard error of D was about

Table 1 Diffusion coefficient of a polystyrene latex (d = 109 nm) determined at 25°C at various wavelengths

Wavelength, λ (nm)	Diffusion coefficient $D \times 10^8$ (cm^2/sec)
476	4.06
531	4.32
568	4.31
647	4.31

Table 2 Temperature dependence of the diffusion coefficient of the polystyrene latex (experimental and theoretical)

T	$D \times 10^8$ (cm^2/sec)		
(°C)	Determined	Calculated	$D_{det.}/D_{cal.}$
24.7	4.31	4.46	0.97
40.2	6.37	6.46	0.99
55.2	8.65	8.77	0.99
70.4	11.5	11.5	1.00

1%; at low molecular weight and low concentration the accuracy was somewhat less.

Since the krypton laser can be tuned over a wide wavelength range, this facility was used to test the performance of our equipment by measuring at four different wavelengths the diffusion of a well-defined polystyrene latex (Dow Chemical; diameter 109 nm) suspended in water. The results, presented in *Table 1*, are in satisfactory agreement. The experimental diffusion coefficient compares very favourably with a value of 4.48×10^{-8} cm^2/sec calculated from the Stokes–Einstein relation ($D = kT/6\pi\eta R$) and even better with a reported[13] literature value of 4.33×10^{-8} cm^2/sec.

For this same latex we also measured the temperature dependence of D at a wavelength of 647 nm (see *Table 2*). A comparison of these values with those calculated from the Stokes–Einstein relation shows that the temperature dependence of D is very well described by that relation.

For the measurements on polystyrene in THF seven samples of atactic polystyrene were used, of weight-average molecular weight M_w ranging from 2.04×10^4 to 1.8×10^6. The samples had a relatively narrow molecular weight distribution with a weight-to-number average molecular weight $M_w/M_n < 1.21$ according to specification. The material was supplied by Pressure Chemical Company and was used as received. Solutions were made up with distilled tetrahydrofuran containing a small amount of antioxidant, this having no effect on the measurements. The solutions were carefully filtered through 0.45 μm filters to remove disturbing dust particles. This turned out to be fully adequate: thorough examination of the shape and angular dependence of the observed correlation functions and the scattering intensity of low molecular weight samples yielded no evidence of any remaining perturbation by residual dust. Most experiments were performed in the low concentration region, i.e. up to 25 g/l for $M_w = 2.04 \times 10^4$ and up to about 10 g/l (1%) for the highest molecular weights. For the sample of $M_w = 4.11 \times 10^5$ the experiments were extended to somewhat higher concentrations (4.3%).

RESULTS

The experimental results for the diffusion of polystyrene in THF at low concentration are plotted in *Figure 1*. All data are obtained at λ = 647 nm at a reference temperature of 24°C. Corrections for small deviations from this average temperature during the experiments have been made according to the Stokes–Einstein relation, amounting to 2% at most.

Within the experimental error the relationship between D and c at a certain molecular weight is linear for all data shown in *Figure 1*. In the case of the highest molecular weight ($M_w = 1.8 \times 10^6$) this is clearer in *Figure 2*, where we have replotted the data on a much larger scale.

In order to obtain an indication of the range of linearity, the measurements on one sample ($M_w = 4.11 \times 10^5$) were extended to somewhat higher concentrations (see *Figure 3*). During this experiment the krypton plasma tube of the ion laser was replaced by an argon tube and subsequently the diffusion was determined from measurements at a wavelength of 488 nm instead of 647 nm. As can be seen from *Figure 3* the two measuring series agree very well. At the highest concentrations the curve starts to deviate from a straight line; evidently the higher terms in the series expansion of equation (1) can no longer be neglected. In this region the experimental correlation function still consists of one single exponential and the angular dependence predicted by equation (2) holds very well. Thus, even with the rather viscous solutions the only detectable cause of line broadening stems from the translational diffusion of the macromolecules.

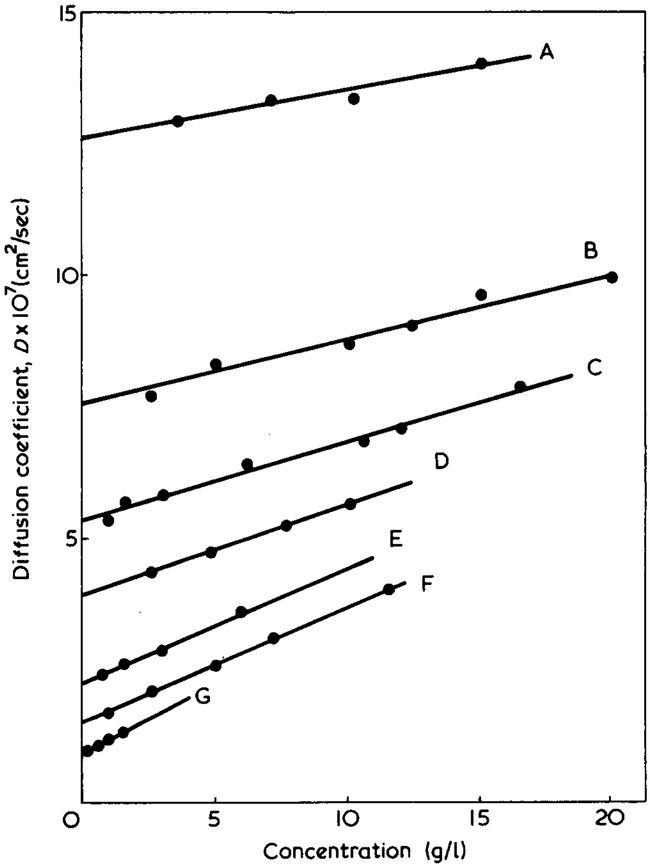

Figure 1 Diffusion coefficient D of polystyrene in tetrahydrofuran at 24°C as a function of concentration at various molecular weights: A, 20 400; B, 51 000; C, 97 200; D, 160 000; E, 411 000; F, 860 000; G, 1 800 000

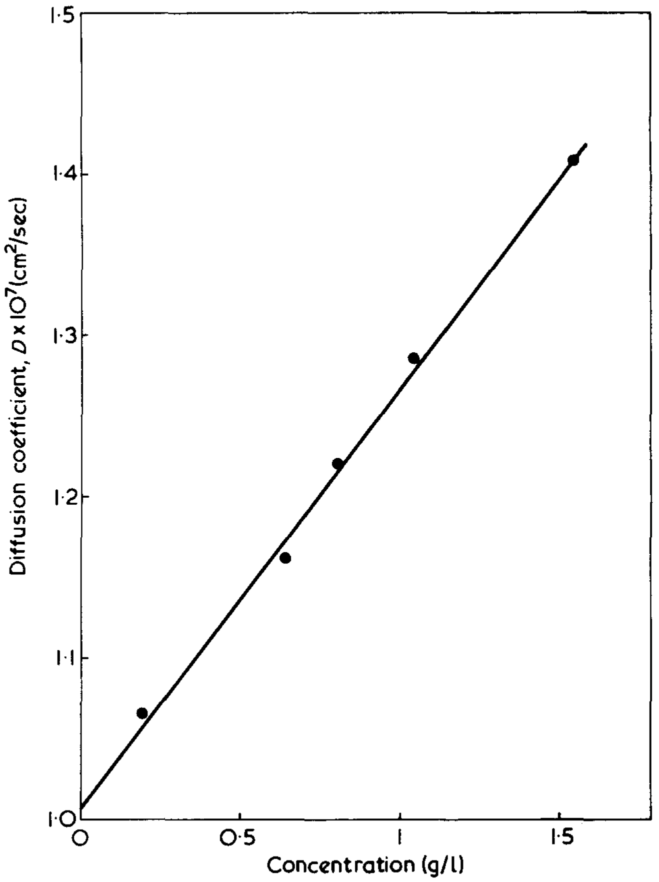

Figure 2 Concentration dependence of the diffusion coefficient of polystyrene in tetrahydrofuran at M_w = 1.8 x 10^6

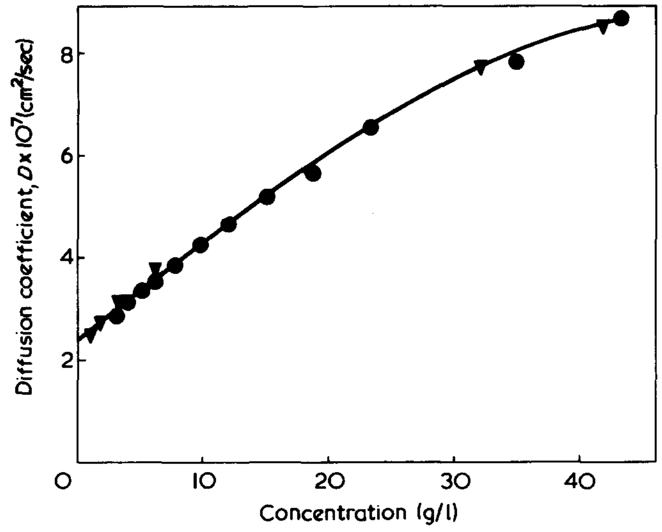

Figure 3 Concentration dependence of the diffusion coefficient of polystyrene in tetrahydrofuran at M_w = 4.11 x 10^5: ●, at 488 nm, argon tube; ▼; at 647 nm, krypton tube

DISCUSSION

Diffusion coefficient at infinite dilution

Extrapolated values of D at $c = 0, D_0$, and the relative slope of the plots in *Figure 1*, k_D, have been obtained from a least-squares fit. The results are presented in *Table 3* and shown graphically in *Figure 4*. For the diffusion coefficient a double-logarithmic plot has been chosen to emphasize the fact that D_0 is proportional to a power of M:

$$D_0 = k_T M_w^{-b} \tag{3}$$

Values of $k_T = 3.45 \times 10^{-4}$ cm²/sec and $b = 0.564$ are obtained with standard deviations of 0.18×10^{-4} and 0.004 respectively. The experimental values of D_0 differ from those calculated on the basis of equation (3) and the given values of k_T and b by at most 2%.

According to thermodynamic theories, the parameter b is related to the corresponding exponent a in the Mark–Houwink relationship for the intrinsic viscosity, as

$$b = (1 + a)/3 \tag{4}$$

The value of $a = 0.692$ calculated from b agrees quite well with the frequently cited value of 0.70 obtained by Benoit *et al.*[14] and many other reported values which, with a few exceptions, all lie in the range 0.68 to 0.70.

Concentration dependence of D

It is evident from the experimental results in *Figure 1* that the concentration dependence of D can be approximated by a linear relationship over a relatively large concentration range, at least up to about c = 20 g/l for the lower molecular weights. This result confirms the recent findings[7–9] on some comparable systems (e.g. polystyrene in butanone). Our data do not yield any evidence suggesting a more complicated behaviour with a concentration-independent region at very low concentration[4].

The relative change of the diffusion coefficient with

Table 3 Diffusion coefficient at infinite dilution, D_0, and the linear coefficient of the concentration dependence of D, k_D, as a function of molecular weight for polystyrene in tetrahydrofuran

M_w	$D_0 \times 10^7$ (cm²/sec)	k_D (l/g)
1 800 000	1.01	0.264
860 000	1.59	0.136
411 000	2.35	0.091
160 000	3.99	0.044
97 200	5.43	0.028
51 000	7.65	0.016
20 400	12.7	0.007

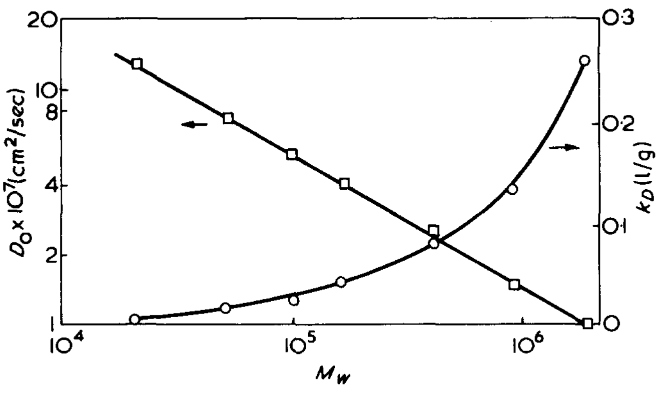

Figure 4 Diffusion coefficient of polystyrene in tetrahydrofuran at infinite dilution, D_0, and the linear coefficient of the concentration dependence of D, k_D, as functions is of molecular weight

Table 4 Values of the second virial coefficient A_2 for polystyrene in THF calculated using the experimental concentration dependence of D in the Pyun–Fixman relation (see equation 5)

		$k_f^{\Phi} = 2.23$		$k_f^{\Phi} = 5$	
M_w	k_D	k_f	$10^4 A_2$	k_f	$10^4 A_2$
1 800 000	264	328	1.6	735	2.8
860 000	136	174	1.8	390	3.0
411 000	91	114	2.5	255	4.2
160 000	44	60	3.2	135	5.6
97 200	28	38	3.3	85	5.8
51 000	16	27	4.1	59	7.3
20 400	7	14	5.1	31	9.3

k_D and k_f in cm^3/g; A_2 in cm^3 mol/g^2

concentration, represented by the value of the parameter k_D, is positive over the whole of the molecular weight range investigated. Hence it may be concluded that the increase of the friction which counteracts the diffusion process is by far outweighed by the even larger increase in the thermodynamic driving forces. However, k_D shows a remarkably strong variation with molecular weight. At $M = 2.04 \times 10^4$ and a concentration of 10 g/l the relative departure of D from D_0 is only 7%, while at $M = 1.8 \times 10^6$ and the same concentration, the diffusion coefficient has changed by about 260% (using linear extrapolation)! Hence, especially at the higher molecular weights, great care is needed when interpreting measurements taken at one single concentration.

A comparison of k_D with theoretical expressions is hampered by the fact that all these expressions contain the second virial coefficient A_2, for which no experimental data are available in the present case. In the Pyun–Fixman[11] approximation for instance (other theories[10,12] lead to analogous relationships), the theoretical expression for k_D becomes:

$$k_D = 2A_2M - k_f^{\Phi}\frac{N_aV_h}{M} - v_2 \tag{5}$$

where V_h is the hydrodynamic volume per macromolecule (see the next section), v_2 the partial specific volume and N_a Avogadro's number. The second term on the right-hand side of equation (5) is an expression for the coefficient of the linear term k_f in a series expansion of the friction coefficient. The crucial point in equation (5) is the precise value of the parameter k_f^{Φ}, which varies from 2.23 for θ-conditions to a hard sphere value of 7.16.

We have used equation (5) to calculate A_2, inserting our experimental values for k_D and the hydrodynamic volume evaluated from the hydrodynamic radius for diffusion R_h^D (as discussed in the next section). Some results are given in *Table 4* for $k_f^{\Phi} = 2.23$ and for the intermediate value of $k_f^{\Phi} = 5$. Comparing these results for THF with those for another good solvent, toluene (where $A_2 = 1.9 \times 10^{-4}$ and 5.2×10^{-4} cm^3 mol/g^2 at $M = 1.8 \times 10^6$ and 2.04×10^4 respectively), we note that the calculated values of A_2 are of the right order of magnitude and so is the molecular weight dependence. For determination of the best value of k_f^{Φ} and for a comparison with other theoretical expressions, experimental data on A_2 for polystyrene in THF are required.

Hydrodynamic radius

With the experimental values of D_0 and the Stokes–Einstein relation for diffusion, an equivalent hydrodynamic radius R_h^D at infinite dilution can be calculated, according to:

$$R_h^D = kT/6\pi\eta_0D_0 \tag{6}$$

where k is Boltzmann's constant, T the absolute temperature and η_0 the viscosity of the solvent. The results are presented in *Table 5*. In the same Table we have included some other parameters: the hydrodynamic radius R_h^{η} derived from viscosity measurements[14] ($R_h^{\eta} = [3[\eta]M/10\pi N_a]^{1/3}$, the intrinsic viscosity $[\eta] = 1.41 \times 10^{-2} M^{0.70}$ cm^3/g) and the unperturbed-radius of gyration R_g^0 obtained from light scattering measurements in θ-solvents, as found in ref 15. There appears to be hardly any difference between R_h^D and R_h^{η}, and their ratio is almost independent of molecular weight, as was already evident from the consistencies of parameters a and b in the first section of this Discussion. The hydrodynamic volumes used in equation 5 were derived from R_h^D, with $V_h = 4\pi/3(R_h^D)^3$.

According to the Kirkwood–Riseman[16] theory both hydrodynamic radii, R_h^D and R_h^{η}, are proportional to the radius of gyration, and their ratio is given by:

$$R_h^D/R_h^{\eta} = \frac{0.665\,R_g}{0.875\,R_g} = 0.76 \tag{7}$$

Clearly, the assumptions of the Kirkwood–Riseman theory, which is based on a polymer coil with an 'ideal' segment distribution (random flight statistics), are not fulfilled for polystyrene in THF. This may be due to excluded volume effects and polymer–solvent interactions, which will lower the segment density of the coil and make it more permeable to the solvent. The effect may be different for diffusion and viscosity.

In the literature we found some measurements on polystyrene in other solvents: the θ-solvent cyclohexane and the rather good solvent butanone and it is very interesting to compare the various results. This can be done from *Table 6* for the highest and lowest molecular weight of our samples. In cyclohexane R_h^D and R_h^{η} are both proportional to $M^{1/2}$, as predicted by theory, and consequently their ratio is constant. For butanone this ratio changes with molecular weight. In both cases the ratios differ considerably from the value of 0.78 predicted by the Kirkwood–Riseman theory. The hydrodynamic radii in the very good solvent THF are by far the largest.

All the preceding remarks concerning the hydrodynamic radii refer to infinite dilution. At finite concentrations the hydrodynamic radius in a good solvent such as THF will decrease owing to the increase in the unfavourable polymer–

Table 5 The hydrodynamic radii R_h^D and R_h^{η} in THF and the unperturbed radius of gyration R_g^0 of polystyrene

M_w	R_h^D (nm)	R_h^{η} (nm)	R_g^0 (nm)	R_h^D/R_g^0
1 800 000	47.1	46	36.7	1.28
860 000	29.8	30	25.4	1.18
411 000	20.2	20	17.5	1.15
160 000	11.9	12	10.9	1.09
97 200	8.7	8.8	8.5	1.02
51 000	6.2	6.1	6.2	1.00
20 400	3.7	3.6	3.9	0.95

Table 6 Comparison of hydrodynamic radii of polystyrene in various solvents

Solvent	Tetrahydrofuran	Butanone	Cyclohexane
D_0 (cm^2/sec)	$3.45 \times 10^{-4} M_w^{-0.564}$ (this work)	$5.5 \times 10^{-4} M_w^{-0.561}$ (ref 8)	$1.3 \times 10^{-4} M_w^{-0.497}$ (ref 7)
$[\eta]$ (cm^3/g)	$1.41 \times 10^{-2} M_w^{0.70}$ (ref 14)	$3.9 \times 10^{-2} M_w^{0.58}$ (ref 15)	$8.4 \times 10^{-2} M_w^{0.50}$ (ref 15)
R_h^D (nm)	$1.37 \times 10^{-2} M_w^{0.564}$	$0.99 \times 10^{-2} M_w^{0.561}$	$2.31 \times 10^{-2} M_w^{0.497}$
R_h^η (nm)	$1.31 \times 10^{-2} M_w^{0.567}$	$1.84 \times 10^{-2} M_w^{0.523}$	$2.37 \times 10^{-2} M_w^{0.500}$

	Tetrahydrofuran			Butanone			Cyclohexane		
M_w	R_h^D	R_h^η	R_h^D/R_h^η	R_h^D	R_h^η	R_h^D/R_h^η	R_h^D	R_h^η	R_h^D/R_h^η
1 800 000	47.1	45.8	1.03	32.0	36.1	0.89	29.7	31.8	0.93
20 400	3.7	3.6	1.03	2.6	3.4	0.76	3.2	3.38	0.94

polymer interactions, the precise reduction being unknown for this system. However, by assuming the radius to remain constant, an appropriate estimation of the total hydrodynamic volume of the macromolecules at a given concentration can be obtained. From such an estimation it turns out that, in most of our measuring series plotted in *Figure 1*, there must already be a considerable overlap of the coils. Nevertheless, this has hardly any effect on the concentration dependence of the diffusion coefficient, which remains linear over the whole indicated region.

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